

Vapor-Liquid Equilibria of Acetone-Cyclohexane and Acetone-Isopropanol Systems at 25°C

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Vapor-liquid equilibrium data are reported for the binary systems acetone-cyclohexane and acetone-isopropanol at 25°C. The acetone-cyclohexane system forms an azeotrope at 74.2 mol % acetone. Values of excess Gibbs free energies and excess volumes are presented and correlated by the Redlich-Kister equation.

Vapor-liquid equilibria at 25°C for the two binary systems, acetone-isopropanol and acetone-cyclohexane, were measured by a circulation method. The experimental equilibrium data, together with the liquid activity coefficients and excess Gibbs free energies, are presented. For the acetone-isopropanol system, equilibrium pressure and composition data have been presented by Hala et al. (2), which they calculated from the pressure-composition data of Parks and Chaffee (7). The present work is compared with these data. No vapor-liquid equilibrium data at 25°C have been reported in the literature for the system acetone-cyclohexane. Also, the excess volumes for the two systems are presented, calculated from experimentally determined densities.

Experimental

The method and equipment used in this study are similar to those described earlier by Polak et al. (8).

A circulation still of 120-cm³ capacity was used for the determination of vapor-liquid equilibrium compositions. Pressure was adjusted manually to obtain the desired temperature in the equilibrium chamber. The boiling of the liquid was continued for 3 hr at the desired temperature (25°C) and then discontinued by a sudden increase of pressure to atmospheric. Samples of the liquid and the condensed vapor phase were taken for analysis. The analyses of both phases were made by measuring their refractive indices at 25°C with a Bausch and Lomb Abbe-3L refractometer. The temperature of the still head, as measured with a calibrated Beckmann thermometer, was maintained within ±0.005°C, and the pressure, as measured with a Texas Instrument pressure gage, was read with a precision of ±0.04 mm Hg.

Refractive indices measured within ±0.00005 for the binary samples prepared to make the calibration curves were correlated by the equation:

$$\eta_D = x_1\eta_{D1} + x_2\eta_{D2} + x_1x_2(Ax_1 + Bx_2 - Cx_1x_2) \quad (1)$$

where η_D is the refractive index of the mixture, and $\eta_{D(1)}$ and $\eta_{D(2)}$ are the refractive indices for the components 1 and 2, respectively. Constants A, B, and C were obtained by the method of least squares. Eleven compositions were used in preparing the calibration curve for each system. The average absolute percentage deviation between the measured refractive index and the value computed by Equation 1 was 0.03 for the acetone-cyclohexane system and 0.004 for the acetone-isopropanol system. These small deviations indicate that the composition-refractive index data are adequately represented by Equation 1.

The estimated precision of the analyses of the equilibrium mixtures is ±0.00075 mole fractions for the system acetone-cyclohexane and ±0.005 mole fraction for the system acetone-isopropanol.

Densities of binary samples at 25°C for the two systems were determined from mixtures of the degassed liquids by use of an Anton Paar precision density meter DMA 02C with a precision of ±0.00005 g/cm³. Both systems showed a minimum on the density-composition curve. Excess volumes, determined from the density measurements, have an estimated uncertainty of ±0.005 cm³ mol⁻¹ for both systems.

Materials

Acetone and isopropanol were gc-spectrophotometric quality, supplied by J. T. Baker Chemical Co., and cyclohexane was spectroquality from Matheson Coleman & Bell. All chemicals were used without further purification. Physical properties of these materials are compared with literature values in Table I.

Results

The equilibrium pressures and composition of the liquid and vapor phases, along with the calculated Raoult's law activity coefficients and molar excess Gibbs free energies, are presented in Table II. The acetone-cyclohexane system forms an azeotrope at a composition of 74.2 mol % acetone. Literature data indicate that at 53°C, an azeotrope exists at 68.2 mol % of acetone (3).

The activity coefficients were calculated from the equation

$$\gamma_i = \frac{y_i P}{x_i P_i^0} + \exp \left[(B_{ii} - v_i^0)(P - P_i^0)/RT + (1 - y_i)^2 P \delta / RT \right] \quad (2)$$

where

$$\delta = 2B_{12} - B_{11} - B_{22} \quad (3)$$

Table I. Physical Properties of Pure Components at 25°C

	Acetone	Cyclohexane	Isopropanol
Density, g/cm ³			
Experimental	0.78554	0.77291	0.78092
Literature	0.7855 (7)	0.77375 (13)	0.78091 (13)
	0.78508 (13)		
Refractive index			
Experimental	1.3566	1.4233	1.3744
Literature	1.35662 (13)	1.4233 (13)	1.3743 (7)
			1.3752 (10)
Vapor pressure, mm Hg			
Experimental	229.55	97.77	44.02
Literature	229.4 (11)	97.85 (14)	44.0 (6)
	226.5 (7)		45.16 (10)
Second virial coefficients, ^a cm ³ mol ⁻¹	-2075 (1)	-1685 (1)	-2354 (4)

^a Extrapolated values.

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Physical constants required for these calculations are given in Table I. The second virial coefficients at 25°C were obtained by graphical extrapolation of literature values. The mixed virial coefficients were estimated by the correlation of O'Connell and Prausnitz (5). The molecular parameters used were those reported in ref. 5, and the critical constants used in the calculations were those obtained from Riddick and Bunger (10).

The Gibbs excess free energy is given by the equation

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

Numerical values of the two systems are shown in Figure 1, where the solid line represents the G^E values correlated by use of Equation 5:

$$G^E = x_1(1 - x_1) \sum_{i=1}^3 C_i (1 - 2x_1)^{i-1} \quad (5)$$

with the values of C_1 , C_2 , C_3 given below. Here, x_1 represents the mole fraction of acetone.

The coefficients in Equation 5 were determined by a least-squares fitting procedure. The resulting coefficients in the order C_1 , C_2 , C_3 for the system acetone-cyclohexane are 4527 ± 6 , 345 ± 15 , and 678 ± 27 with a standard deviation of 4.1 J mol^{-1} . For the acetone-isopropanol system, the precision of the data warrants the use of only two constants in Equation 5. For this system, $C_1 = 2498 \pm 68$, and $C_2 = 863 \pm 189$, with a standard deviation of 41 J mol^{-1} . The estimated uncertainties in G^E based on the precision of the measured quantities is in the mean 3.0 and 28.5 J mol^{-1} for the systems acetone-cyclohexane and acetone-isopropanol, respectively.

The thermodynamic consistency of the data was tested by the area test of Redlich and Kister (9). The difference between the positive and negative areas of the $\ln(\gamma_1/\gamma_2)$ vs. x_1 curve expressed as a percentage of the total area is about 2.5% for the system acetone-cyclohexane and 5% for the system acetone-isopropanol. This is, in the case of acetone-isopropanol, a considerable improvement, since the area test for the data of Parks and Chaffee (7) shows a difference of positive and negative areas of over 50%.

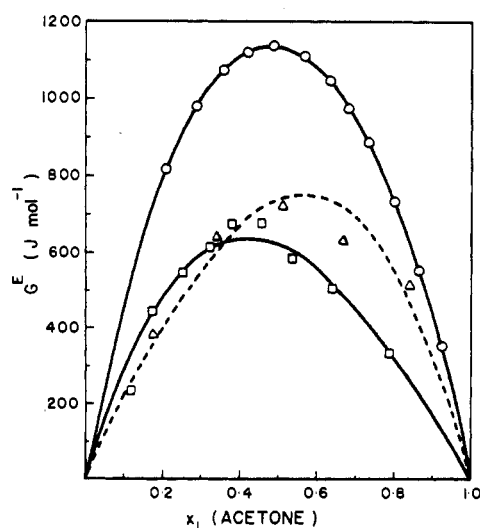


Figure 1. Molar excess Gibbs free energies at 25°C

○ Acetone(1)-cyclohexane(2)
 □ Acetone(1)-isopropanol(2)
 △ Acetone(1)-isopropanol(2), ref. 7

Table II. Vapor-Liquid Equilibrium Data at 25°C

x_1	y_1	P, mm Hg	γ_1	γ_2	G^E , J mol ⁻¹
Acetone(1)-cyclohexane(2)					
0.2077	0.6184	231.91	3.013	1.134	815
0.2868	0.6452	242.89	2.381	1.226	977
0.3520	0.6609	249.17	2.037	1.323	1070
0.4158	0.6737	253.06	1.784	1.434	1119
0.4847	0.6867	256.38	1.580	1.582	1135
0.5654	0.7025	259.16	1.400	1.800	1105
0.6311	0.7156	260.76	1.285	2.041	1044
0.6809	0.7272	261.58	1.214	2.270	976
0.7316	0.7403	262.10	1.522	2.575	886
0.7990	0.7681	261.26	1.091	3.062	730
0.8610	0.7976	258.97	1.042	3.836	551
0.9209	0.8536	253.48	1.021	4.782	354
Acetone(1)-isopropanol(2)					
0.117	0.579	93.48	2.061	1.012	235
0.171	0.622	103.17	1.730	1.110	446
0.249	0.695	125.50	1.547	1.161	547
0.322	0.736	138.78	1.398	1.233	619
0.381	0.766	150.60	1.333	1.299	672
0.455	0.797	161.54	1.243	1.375	675
0.532	0.843	173.53	1.207	1.335	583
0.638	0.877	185.32	1.115	1.448	504
0.784	0.928	202.43	1.047	1.564	327

Table III. Excess Molar Volumes at 25°C

Acetone(1)-cyclohexane(2)		Acetone(1)-isopropanol(2)	
x_1	V^E , cm ³ mol ⁻¹	x_1	V^E , cm ³ mol ⁻¹
0.1688	0.645	0.121	0.136
0.3068	0.930	0.206	0.178
0.4152	1.060	0.297	0.271
0.4745	1.082	0.420	0.316
0.6159	1.043	0.518	0.320
0.6790	0.974	0.587	0.311
0.7866	0.771	0.667	0.282
0.9294	0.323	0.790	0.208
		0.878	0.145

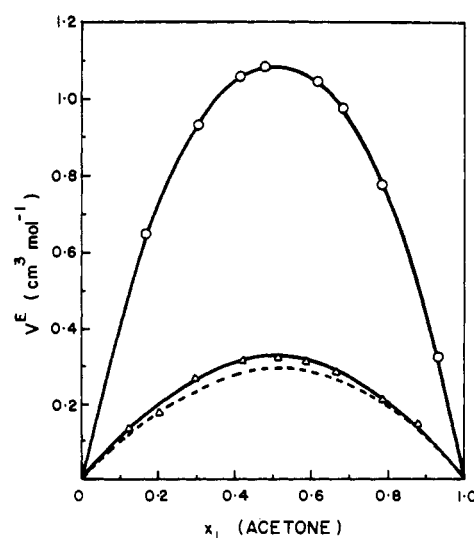


Figure 2. Molar excess volumes at 25°C

○ Acetone(1)-cyclohexane(2)
 △ Acetone(1)-isopropanol(2)
 --- Acetone(1)-isopropanol(2), data calculated from the equation given in ref. 12

The densities of binary mixtures were used to calculate the excess volumes of the two systems. Numerical values are listed in Table III and are shown in Figure 2. Excess volumes were also expressed by the right-hand side of Equation 5, and this equation was used to generate the solid lines in Figure 2. For the acetone-cyclohexane system, the constants C_1 , C_2 , and C_3 are 4.348 ± 0.009 , -0.103 ± 0.024 , and 0.623 ± 0.066 , respectively, with a standard deviation of $0.005 \text{ cm}^3 \text{ mol}^{-1}$. The excess volume at $x_1 = 0.5$ is $V_{0.5}^E = 1.08 \text{ cm}^3 \text{ mol}^{-1}$. For the acetone-isopropanol system, only one constant was required. Here, $C_1 = 1.271 \pm 0.019$ with a standard deviation of $0.012 \text{ cm}^3 \text{ mol}^{-1}$. At $x_1 = 0.5$, $V_{0.5}^E = 0.32 \text{ cm}^3 \text{ mol}^{-1}$. The data for the acetone-isopropanol system are compared in Figure 2 with those calculated from the equation given by Thacker and Rowlinson (12).

Nomenclature

A, B, C = constants in Equation 1
 B_{ii} = second virial coefficient of pure component i , $\text{cm}^3 \text{ mol}^{-1}$
 B_{12} = cross virial coefficient, $\text{cm}^3 \text{ mol}^{-1}$
 C_1, C_2, C_3 = coefficients in Redlich-Kister Equation 5, J mol^{-1} for G^E and $\text{cm}^3 \text{ mol}^{-1}$ for V^E
 G^E = molar excess Gibbs free energy, J mol^{-1}
 P = total vapor pressure, mm Hg
 P_i° = vapor pressure of pure component i , mm Hg
 R = gas constant
 T = absolute temperature, K
 V^E = molar excess volume, $\text{cm}^3 \text{ mol}^{-1}$
 v_i° = molar volume of pure component, $\text{cm}^3 \text{ mol}^{-1}$

x_i = mole fraction of component i in liquid phase
 y_i = mole fraction of component i in vapor phase

Greek Letters

γ_i = activity coefficient of component i in liquid phase
 δ = difference of virial coefficients as defined by Equation 3, $\text{cm}^3 \text{ mol}^{-1}$
 η_D = refractive index of the mixture
 η_{Di} = refractive index of pure component i

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Solubility of Nitrous Oxide in Sodium Carbonate-Sodium Bicarbonate Solutions at 25°C and 1 Atm

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Solubility of nitrous oxide in sodium carbonate-sodium bicarbonate solutions of various carbonation ratios and of various ionic strengths was measured at 25°C and 1 atm. The experimental results were analyzed on the basis of the method proposed by Danckwerts and Gillham for the solubility of the gas in mixed electrolyte solutions.

Aqueous solutions of alkali carbonate-bicarbonate are widely used in the chemical industry for the removal of the acid gases, such as carbon dioxide, hydrogen sulfide, sulfur dioxide, and chlorine. Therefore, knowledge of the gas solubility in these solutions is important in the rational design of absorption equipment. Since the acid gas reacts in carbonate-bicarbonate solutions, it is not possible to measure the gas solubility by conventional methods. However, in the case of electrolyte solutions, the solubility of the reacting gas can be estimated from that of the nonreacting gas in the same solutions by the method of van Krevelen and Hoftijzer (10). In this paper the data on the solubility of nitrous oxide in sodium car-

bonate-sodium bicarbonate solutions of various compositions and of various ionic strengths are reported.

Theory

The physical solubility of a gas in aqueous electrolyte solutions can be correlated by the following expression:

$$\log(A^*/A_w^*) = -k_s I \quad (1)$$

where A^* and A_w^* are the physical solubilities in the solution and in water, respectively, and I is the ionic strength of the solution defined by

$$I = \frac{1}{2} \sum c_i z_i^2 \quad (2)$$

c_i being the concentration of ions of valency z_i . The coefficient k_s is the salting-out parameter and is expressed as the sum of the contributions owing to the positive and negative ions present and the dissolved gas (10):

$$k_s = i_+ + i_- + i_g \quad (3)$$

The values of i for various ions and gases were reported by van Krevelen and Hoftijzer (10), Barrett (1), and Onda et al. (8). However, the value of i_- for bicarbonate ion has not been known.

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