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Total-Pressure Vapor–Liquid Equilibrium Data for Binary Systems of Acetone with Isopropylbenzene and Isopropenylbenzene

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Total-pressure vapor–liquid equilibrium data are reported for the acetone + isopropylbenzene system at 293.15, 345.15, and 387.15 K and the acetone + isopropenylbenzene system at 295.65, 331.90, and 372.15 K. The experimental *PTx* data were reduced to y_i, γ_i, and G^E values by both the Mixon et al. and the Barker methods but only the Mixon et al. results are reported. Seven G^E correlations were tested in the Barker data reduction. The Barker and Mixon et al. results are compared.

Introduction

This paper reports vapor–liquid equilibrium data for two acetone binaries with similar second components—isopropylbenzene (cumene) and isopropenylbenzene (α-methylstyrene). Creation of the double bond in the isopropyl group decreases appreciably the level of nonideality of the acetone–hydrocarbon mixtures.

The apparatus and techniques used for the experimental measurements, along with the standard states used and the defining equation for the activity coefficient, have been presented in a previous paper (*1*).

Chemicals Used

The sources and purities of the chemicals used are listed in Table I. The chemicals were distilled under vacuum over molecular sieves just prior to loading the equilibrium cells. A Vigreux column (25 mm o.d. and 470 mm long) was used. The first and last portions of each distillate were discarded. The middle portion was collected under dry nitrogen in amber bottles for transfer to the cell-loading operation.

For the acetone + isopropenylbenzene system, 100 ppm of benzoquinone was added to each equilibrium cell containing the hydrocarbon to inhibit polymerization.

None of the compounds exhibited any signs of degradation during the measurements. The cell pressures were stable with respect to time at all temperatures. The acetone + isopropylbenzene liquids were perfectly clear when emptied from the cells after the last isotherm. The isopropenylbenzene-system liquids were also colorless except for the very light yellowish tinge caused by the addition of the benzoquinone.

Table II shows that the measured pure-compound vapor pressures for acetone and isopropylbenzene agree well enough with two different evaluated data compilations. The correlations from which the Thermodynamics Research Laboratory (TRL) values for acetone and isopropylbenzene in Table II were calculated are based on data from 10 and 7 literature sources, respectively, with the data of Ambrose et al. (*2*) being the major contributor to the acetone correlation. The literature isopropenylbenzene values come from only Dreisbach and Martin (*3*) with points from six other sources being excluded. The excluded points, with the exception of those from Stull (*4*), were single scattered points but they all (including the Stull values) fell below the Dreisbach and Martin values at the two temperatures shown, which indicates that the TRL-compilation values in Table II may be high. Hence, it is highly probable that the isopropenylbenzene used in the vapor–liquid equilibrium data measurements did not undergo any significant polymerization.

Table I. Chemicals Used

component	supplier	purity, %
acetone	Burdick and Jackson	99.9
isopropylbenzene	Phillips Petroleum	99.9
isopropenylbenzene	Monsanto	99.9

Table II. Comparison of Measured Vapor Pressures with Literature Values

component	T, K	vapor press., kPa measd	lit. TRL[a]	lit. TRC[b]
acetone	293.15	24.669	24.739	24.656
	295.65	27.586	27.638	27.524
	331.90	110.74	110.97	110.13
	345.15	169.03	169.68	168.56
	372.15	362.0	362.59	361.7
	387.15	526.1	525.7	525.5
isopropylbenzene	293.15	0.461	0.451	0.447
	345.15	7.026	6.927	6.927
	387.15	33.41	33.25	33.24
isopropenylbenzene	295.65	0.335		
	331.90	2.202	2.402	
	372.15	12.733	13.112	

[a] Evaluated data compilations from the Thermodynamic Research Laboratory, Washington University. [b] Evaluated data compilations from the Thermodynamics Research Center, Texas A&M University.

Table III. Experimental P vs. x_1 Values for the Acetone (1) + Isopropylbenzene (2) System

293.15 K			345.15 K			387.15 K		
	P, KPA			P, KPA			P, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
0.0	0.461	0.461	0.0	7.026	7.031	0.0	33.41	33.40
0.0433	2.807	2.802	0.0430	19.857	19.841	0.0425	66.53	66.55
0.0891	4.841	4.851	0.0885	31.98	31.99	0.0877	99.53	99.45
0.1512	7.159	7.158	0.1505	46.57	46.59	0.1491	140.07	140.22
0.2164	9.177	9.168	0.2160	60.01	59.99	0.2146	179.40	179.29
0.2964	11.295	11.289	0.2951	74.13	74.14	0.2930	221.32	221.30
0.3997	13.599	13.621	0.3986	90.27	90.34	0.3969	271.52	271.66
0.4924	15.435	15.425	0.4914	103.37	103.29	0.4899	312.9	312.7
0.5958	17.240	17.243	0.5950	116.75	116.68	0.5934	355.0	355.1
0.6938	18.894	18.887	0.6931	128.75	128.84	0.6920	394.2	394.1
0.7830	20.408	20.404	0.7826	139.78	139.92	0.7818	430.2	430.1
0.8556	21.708	21.707	0.8554	149.29	149.20	0.8548	460.5	460.6
0.9322	23.186	23.199	0.9320	159.57	159.43	0.9317	494.4	494.3
0.9559	23.688	23.693	0.9551	162.65	162.66	0.9549	504.8	504.9
1.0000	24.669	24.658	1.0000	169.03	169.12	1.0000	526.1	526.1

Table IV. Experimental P vs. x_1 Values for the Acetone (1) + Isopropenylbenzene (2) System

295.65 K			331.90 K			372.15 K		
	P, KPA			P, KPA			P, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
0.0	0.335	0.334	0.0	2.202	2.203	0.0	12.733	12.726
0.0459	2.497	2.503	0.0458	10.359	10.349	0.0454	36.41	36.47
0.0897	4.373	4.362	0.0894	17.444	17.451	0.0888	57.70	57.46
0.1385	6.239	6.241	0.1381	24.689	24.704	0.1374	79.01	79.41
0.2112	8.720	8.735	0.2108	34.42	34.43	0.2098	110.00	109.76
0.2955	11.294	11.273	0.2950	44.50	44.43	0.2940	142.00	141.88
0.3958	13.960	13.966	0.3952	55.12	55.16	0.3937	176.09	176.29
0.4914	16.277	16.288	0.4909	64.48	64.51	0.4896	206.55	206.62
0.5921	18.535	18.541	0.5917	73.62	73.65	0.5906	236.73	236.68
0.6942	20.732	20.704	0.6938	82.56	82.44	0.6930	266.64	266.36
0.7794	22.486	22.496	0.7791	89.74	89.77	0.7785	291.2	291.3
0.8378	23.750	23.762	0.8376	94.89	94.95	0.8370	308.7	308.9
0.9143	25.503	25.500	0.9141	102.08	102.09	0.9139	333.0	333.1
0.9527	26.422	26.416	0.9526	105.94	105.88	0.9525	346.0	345.8
1.0000	27.59	27.59	1.0000	110.74	110.76	1.0000	362.0	362.1

Experimental Data

Tables III and IV present the experimental *PTx* data. The "smooth" pressure values reported there are from the least-squares cubic splined fits used to provide the evenly spaced

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Table V. Calculated Data for the Acetone (1) + Isopropylbenzene (2) System at 293.15 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 73.51 COMPONENT 2 = 139.48
VIRIAL COEFFICIENTS, ML/MOL: B11 = -1433.3 B12 = -3089.8 B22 = -7491.5

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	0.461	0.461	1.0002	0.9986	0.0	2.4658	1.0000	0.0
0.050	3.125	3.125	0.9982	0.9930	0.8586	2.2057	1.0028	102.93
0.100	5.292	5.292	0.9969	0.9888	0.9199	1.9983	1.0108	192.33
0.150	7.116	7.116	0.9958	0.9853	0.9428	1.8341	1.0232	269.33
0.200	8.691	8.691	0.9949	0.9823	0.9551	1.7001	1.0398	334.75
0.250	10.098	10.098	0.9941	0.9796	0.9630	1.5919	1.0598	389.39
0.300	11.378	11.379	0.9933	0.9772	0.9686	1.5023	1.0833	434.06
0.350	12.549	12.549	0.9926	0.9750	0.9728	1.4253	1.1110	469.14
0.400	13.626	13.626	0.9920	0.9729	0.9761	1.3579	1.1438	494.78
0.450	14.626	14.626	0.9914	0.9710	0.9789	1.2984	1.1823	510.95
0.500	15.564	15.564	0.9909	0.9693	0.9812	1.2458	1.2275	517.57
0.550	16.456	16.455	0.9903	0.9676	0.9833	1.1993	1.2802	514.51
0.600	17.315	17.315	0.9898	0.9660	0.9852	1.1583	1.3418	501.59
0.650	18.156	18.155	0.9893	0.9644	0.9870	1.1226	1.4139	478.59
0.700	18.991	18.991	0.9888	0.9629	0.9887	1.0916	1.4983	445.26
0.750	19.835	19.835	0.9883	0.9613	0.9903	1.0654	1.5977	401.30
0.800	20.701	20.701	0.9878	0.9597	0.9920	1.0436	1.7154	346.35
0.850	21.603	21.603	0.9873	0.9581	0.9938	1.0263	1.8568	279.96
0.900	22.554	22.554	0.9867	0.9563	0.9957	1.0132	2.0310	201.49
0.950	23.568	23.568	0.9861	0.9545	0.9977	1.0044	2.2617	109.71
1.000	24.658	24.658	0.9855	0.9525	1.0000	1.0000	2.8051	0.0

Table VI. Calculated Data for the Acetone (1) + Isopropylbenzene (2) System at 345.15 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 79.45 COMPONENT 2 = 147.32
VIRIAL COEFFICIENTS, ML/MOL: B11 = -858.4 B12 = -1705.7 B22 = -3628.4

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	7.031	7.031	1.0006	0.9911	0.0	1.9948	1.0000	0.0
0.050	21.800	21.799	0.9943	0.9764	0.6882	1.8657	1.0017	94.10
0.100	34.858	34.857	0.9900	0.9648	0.8120	1.7517	1.0068	178.46
0.150	46.467	46.466	0.9864	0.9546	0.8641	1.6502	1.0155	253.01
0.200	56.880	56.878	0.9832	0.9457	0.8932	1.5605	1.0276	317.81
0.250	66.308	66.306	0.9804	0.9376	0.9120	1.4812	1.0432	372.92
0.300	74.955	74.953	0.9777	0.9303	0.9254	1.4117	1.0624	418.44
0.350	82.997	82.995	0.9753	0.9235	0.9356	1.3509	1.0851	454.53
0.400	90.534	90.531	0.9730	0.9172	0.9438	1.2973	1.1118	481.31
0.450	97.652	97.649	0.9709	0.9112	0.9505	1.2497	1.1430	498.79
0.500	104.436	104.432	0.9688	0.9056	0.9563	1.2075	1.1791	506.91
0.550	110.965	110.961	0.9669	0.9003	0.9615	1.1700	1.2209	505.56
0.600	117.308	117.303	0.9650	0.8951	0.9661	1.1368	1.2694	494.60
0.650	123.528	123.524	0.9631	0.8900	0.9704	1.1076	1.3258	473.81
0.700	129.691	129.687	0.9612	0.8850	0.9745	1.0821	1.3916	442.89
0.750	135.863	135.859	0.9594	0.8801	0.9785	1.0600	1.4691	401.46
0.800	142.108	142.105	0.9575	0.8751	0.9824	1.0414	1.5617	349.02
0.850	148.491	148.488	0.9556	0.8701	0.9864	1.0261	1.6750	284.85
0.900	155.078	155.076	0.9536	0.8650	0.9905	1.0140	1.8203	207.82
0.950	161.932	161.931	0.9515	0.8597	0.9949	1.0052	2.0289	115.67
1.000	169.121	169.121	0.9494	0.8543	1.0000	1.0000	2.6332	0.0

values required by the finite-difference Mixon–Gumowski–Carpenter method (*5*) for reduction of *PTx* data.

Figures 1 and 2 show the experimental data in terms of the pressure deviation P_D from Raoult's law

$$P_D = P - [P_2' + x_1(P_1' - P_2')]$$

where P is the experimental mixture pressure and the P_i' values are the measured pure-component vapor pressures. The deviation pressure plot emphasizes the scatter more than a P vs. x_1 plot but has the disadvantage of not indicating whether an azeotrope exists. Neither of the two systems formed an azeotrope at any of the temperatures covered.

The point symbols in Figures 1 and 2 denote the experimental data points. The curves approximate—sometimes not very closely—the cubic splined fits of those data points. Interpolated values (at 0.025 increments in x_1) from the splined fits are fed to the plotting software which then makes its own fit of the input values. Those fits are often not very good if the curve is irregularly shaped. For example, the discrepancies between the curves and the points at high x_1 values reflect inaccuracies in the arbitrary fits more than scatter in the experimental pressure values. For an accurate determination of how closely the splined fits represent the experimental points, Tables III and IV must be used.

Both systems show positive deviations from Raoult's law and those deviations increase rapidly with temperature over the temperature range covered. The only other characteristic worthy of note is the dip in the P_D curves as the x_1 = 1.0 point is approached.

Table VII. Calculated Data for the Acetone (1) + Isopropylbenzene (2) System at 387.15 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 85.70 COMPONENT 2 = 154.50
VIRIAL COEFFICIENTS, ML/MOL: B11 = -626.4 B12 ■ -1202.1 B22 = -2394.4

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	33.401	33.401	1.0002	0.9751	0.0	1.7596	1.0000	0.0
0.050	72.205	72.202	0.9889	0.9506	0.5478	1.6777	1.0012	87.01
0.100	107.953	107.949	0.9809	0.9306	0.7057	1.6009	1.0050	166.06
0.150	140.790	140.784	0.9740	0.9128	0.7809	1.5282	1.0118	236.76
0.200	170.917	170.912	0.9678	0.8968	0.8252	1.4598	1.0217	298.69
0.250	198.774	198.769	0.9622	0.8823	0.8547	1.3976	1.0346	351.60
0.300	224.854	224.850	0.9570	0.8688	0.8762	1.3423	1.0506	395.49
0.350	249.561	249.558	0.9520	0.8561	0.8929	1.2938	1.0694	430.53
0.400	273.062	273.059	0.9473	0.8442	0.9064	1.2504	1.0915	456.80
0.450	295.484	295.482	0.9429	0.8330	0.9176	1.2111	1.1175	474.22
0.500	316.956	316.955	0.9386	0.8223	0.9273	1.1755	1.1482	482.63
0.550	337.638	337.637	0.9345	0.8122	0.9358	1.1432	1.1842	481.72
0.600	357.765	357.764	0.9305	0.8023	0.9435	1.1141	1.2261	471.20
0.650	377.579	377.579	0.9266	0.7928	0.9506	1.0884	1.2748	450.80
0.700	397.325	397.325	0.9227	0.7834	0.9575	1.0661	1.3309	420.26
0.750	417.246	417.247	0.9187	0.7740	0.9642	1.0472	1.3953	379.33
0.800	437.585	437.585	0.9147	0.7645	0.9708	1.0316	1.4693	327.77
0.850	458.529	458.530	0.9105	0.7549	0.9776	1.0192	1.5551	265.34
0.900	480.187	480.188	0.9062	0.7452	0.9846	1.0099	1.6588	191.48
0.950	502.662	502.663	0.9018	0.7352	0.9919	1.0034	1.7970	104.84
1.000	526.056	526.056	0.8972	0.7252	1.0000	1.0000	2.1181	0.0

Table VIII. Calculated Data for the Acetone (1) + Isopropenylbenzene (2) System at 295.65 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 73.80 COMPONENT 2 = 130.10

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	0.334	0.334	1.0000	0.9997	0.0	1.8432	1.0000	0.0
0.050	2.683	2.683	0.9991	0.9981	0.8812	1.7301	1.0016	71.06
0.100	4.775	4.775	0.9984	0.9967	0.9364	1.6343	1.0062	134.41
0.150	6.659	6.660	0.9978	0.9954	0.9565	1.5512	1.0137	190.34
0.200	8.371	8.371	0.9972	0.9943	0.9671	1.4776	1.0242	239.00
0.250	9.940	9.941	0.9967	0.9933	0.9736	1.4124	1.0377	280.44
0.300	11.399	11.399	0.9962	0.9923	0.9782	1.3553	1.0541	314.80
0.350	12.772	12.773	0.9957	0.9914	0.9816	1.3055	1.0732	342.26
0.400	14.073	14.073	0.9953	0.9905	0.9842	1.2614	1.0956	362.96
0.450	15.308	15.308	0.9949	0.9897	0.9864	1.2218	1.1217	376.87
0.500	16.487	16.487	0.9945	0.9889	0.9882	1.1859	1.1524	383.90
0.550	17.619	17.619	0.9941	0.9882	0.9897	1.1535	1.1883	383.86
0.600	18.712	18.712	0.9937	0.9875	0.9911	1.1240	1.2307	376.49
0.650	19.776	19.776	0.9934	0.9868	0.9923	1.0975	1.2807	361.46
0.700	20.825	20.825	0.9930	0.9861	0.9935	1.0739	1.3397	338.41
0.750	21.874	21.874	0.9927	0.9854	0.9945	1.0536	1.4090	306.97
0.800	22.938	22.938	0.9923	0.9847	0.9956	1.0365	1.4908	266.77
0.850	24.032	24.032	0.9919	0.9840	0.9966	1.0227	1.5880	217.38
0.900	25.167	25.167	0.9916	0.9832	0.9977	1.0121	1.7074	158.19
0.950	26.350	26.350	0.9912	0.9824	0.9988	1.0046	1.8719	87.83
1.000	27.588	27.588	0.9907	0.9816	1.0000	1.0000	2.3850	0.0

Table IX. Calculated Data for the Acetone (1) + Isopropenylbenzene (2) System at 331.90 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 78.00 COMPONENT 2 = 134.80

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	2.203	2.203	0.9998	0.9985	0.0	1.7532	1.0000	0.0
0.050	11.063	11.063	0.9973	0.9939	0.8096	1.6627	1.0013	73.68
0.100	19.086	19.086	0.9953	0.9899	0.8945	1.5813	1.0054	139.91
0.150	26.380	26.381	0.9935	0.9864	0.9272	1.5071	1.0124	198.61
0.200	33.056	33.056	0.9919	0.9831	0.9446	1.4403	1.0221	249.72
0.250	39.223	39.224	0.9904	0.9801	0.9555	1.3807	1.0348	293.26
0.300	44.993	44.993	0.9890	0.9773	0.9631	1.3283	1.0501	329.34
0.350	50.456	50.456	0.9876	0.9746	0.9689	1.2824	1.0680	358.16
0.400	55.654	55.653	0.9863	0.9721	0.9734	1.2416	1.0889	379.84
0.450	60.614	60.614	0.9851	0.9697	0.9770	1.2049	1.1133	394.36
0.500	65.369	65.368	0.9839	0.9674	0.9801	1.1716	1.1419	401.60
0.550	69.946	69.945	0.9828	0.9652	0.9827	1.1412	1.1756	401.36
0.600	74.377	74.375	0.9817	0.9631	0.9850	1.1136	1.2152	393.33
0.650	78.698	78.697	0.9807	0.9610	0.9871	1.0887	1.2620	377.16
0.700	82.968	82.967	0.9796	0.9590	0.9890	1.0666	1.3170	352.46
0.750	87.247	87.246	0.9786	0.9569	0.9909	1.0475	1.3812	318.86
0.800	91.596	91.595	0.9775	0.9548	0.9926	1.0316	1.4560	276.02
0.850	96.074	96.074	0.9764	0.9527	0.9944	1.0189	1.5434	223.61
0.900	100.736	100.736	0.9753	0.9505	0.9962	1.0095	1.6469	161.20
0.950	105.620	105.620	0.9741	0.9482	0.9980	1.0032	1.7790	87.94
1.000	110.763	110.763	0.9728	0.9457	1.0000	1.0000	2.0849	0.0

Reduced Data

Tables V–X list the y_i, γ_i, and G^E values obtained with the Mixon et al. data reduction method (*5*). The equation of state used to estimate the vapor-phase fugacity coefficients for the acetone + isopropylbenzene system was the virial equation with the Tsonopoulos correlation (*6*) for the second virial coefficients. (Those coefficients are given in Tables V–VII.) For acetone + isopropenylbenzene, the Redlich–Kwong equation of state with the Lu modification (*7*) was used. (The Lu

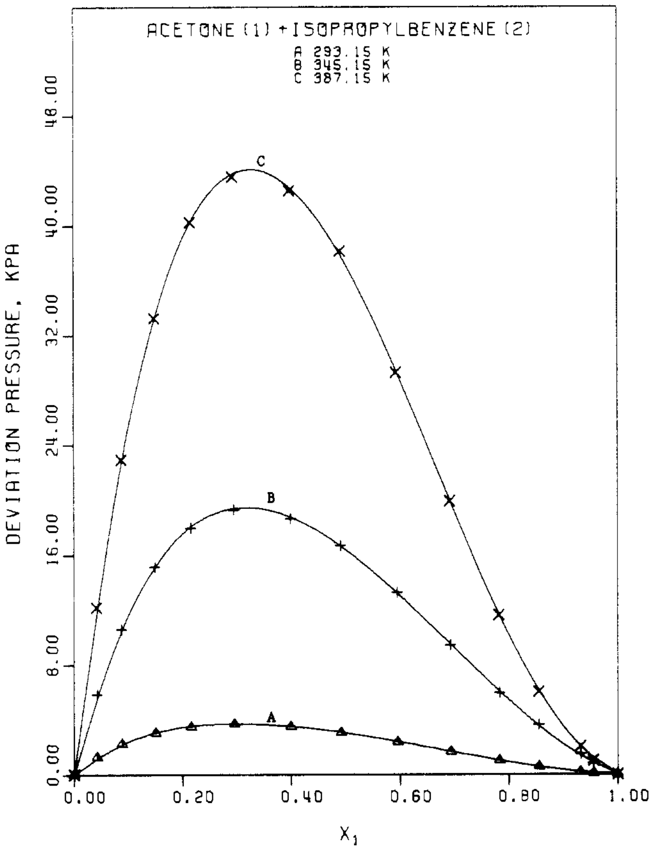

Figure 1. Deviation from Raoult's law for the acetone (1) + isopropylbenzene (2) system.

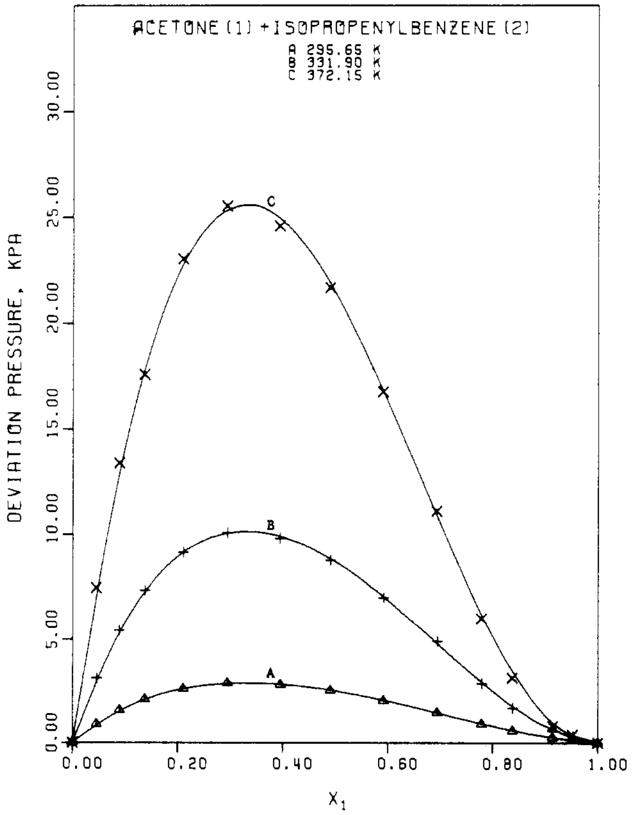

Figure 2. Deviation from Raoult's law for the acetone (1) + isopropenylbenzene (2) system.

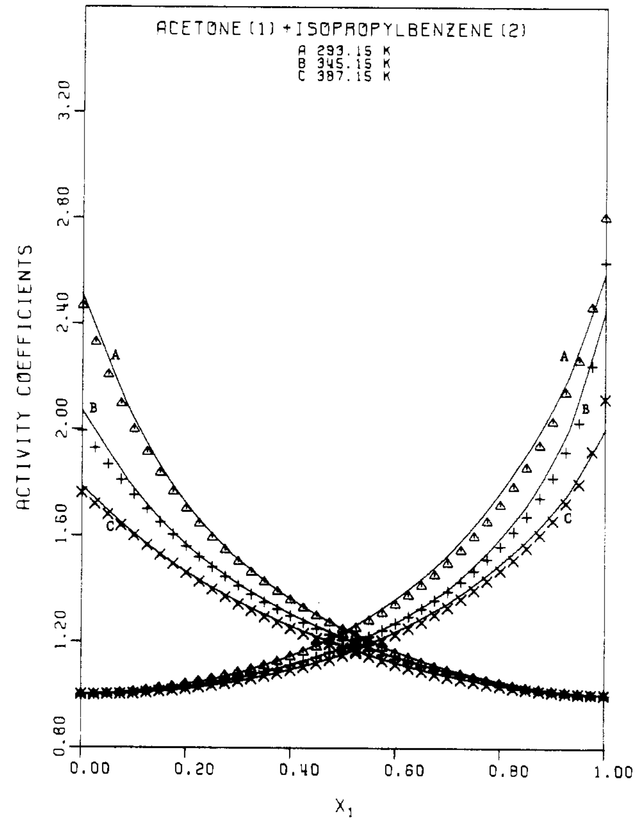

Figure 3. Activity coefficients for the acetone (1) + isopropylbenzene (2) system. Curves from Barker results; points from Mixon et al. method.

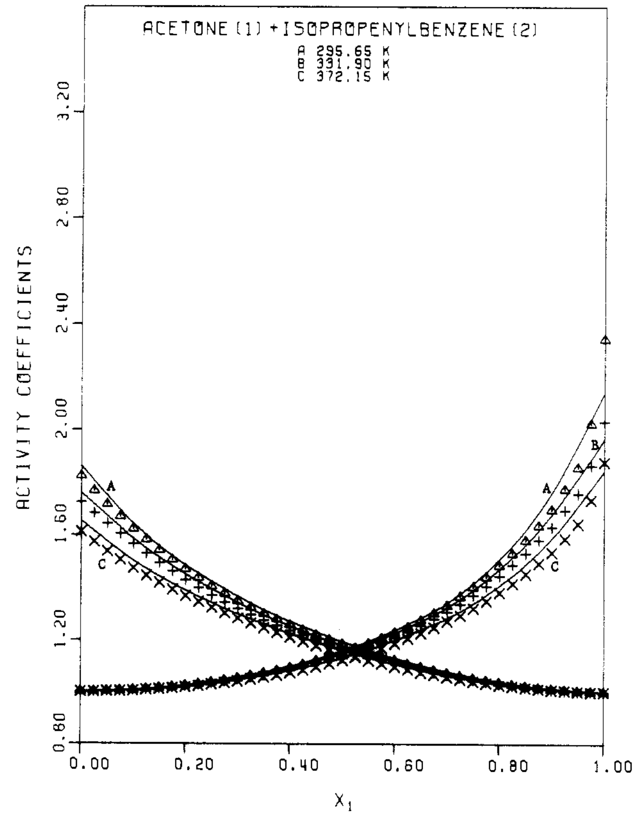

Figure 4. Activity coefficients for the acetone (1) + isopropenylbenzene (2) system. Curves from Barker results; points from Mixon et al. method.

parameters are given in Table XI).

The "experimental" pressure values tabulated in Tables V–X are actually interpolated values from the cubic splined fits of the experimental P vs. x_1 values. (The fidelity with which the splined fits represent the actual experimental P values is shown in Tables III and IV.) The "calculated" pressure values are from the Mixon et al. data reduction method and show how well

Table X. Calculated Data for the Acetone (1) + Isopropenylbenzene (2) System at 372.15 K

LIQUID MOLAR VOLUMES, ML/MOL: COMPONENT 1 = 83.30 COMPONENT 2 = 141.10

	P, KPA		FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		GE
X1	EXPTL	CALC	1	2	Y1	1	2	J/MOL
0.0	12.726	12.726	0.9994	0.9937	0.0	1.6595	1.0000	0.0
0.050	38.783	38.781	0.9936	0.9832	0.6841	1.5697	1.0014	73.86
0.100	62.627	62.624	0.9892	0.9745	0.8121	1.4967	1.0052	139.29
0.150	84.884	84.880	0.9851	0.9666	0.8671	1.4372	1.0110	197.23
0.200	105.793	105.789	0.9813	0.9591	0.8980	1.3852	1.0190	248.18
0.250	125.477	125.471	0.9778	0.9522	0.9179	1.3379	1.0293	292.22
0.300	144.050	144.045	0.9745	0.9456	0.9319	1.2944	1.0423	329.28
0.350	161.631	161.626	0.9713	0.9395	0.9423	1.2542	1.0583	359.20
0.400	178.355	178.349	0.9684	0.9337	0.9505	1.2173	1.0774	381.80
0.450	194.359	194.355	0.9655	0.9281	0.9572	1.1834	1.1001	396.91
0.500	209.780	209.775	0.9628	0.9228	0.9629	1.1526	1.1267	404.32
0.550	224.755	224.752	0.9601	0.9176	0.9677	1.1247	1.1576	403.87
0.600	239.422	239.418	0.9575	0.9126	0.9721	1.0998	1.1933	395.34
0.650	253.917	253.914	0.9549	0.9076	0.9760	1.0777	1.2344	378.54
0.700	268.377	268.375	0.9524	0.9027	0.9797	1.0584	1.2816	353.25
0.750	282.940	282.940	0.9498	0.8977	0.9832	1.0419	1.3358	319.25
0.800	297.743	297.741	0.9472	0.8927	0.9865	1.0281	1.3985	276.24
0.850	312.922	312.921	0.9445	0.8876	0.9898	1.0171	1.4718	223.88
0.900	328.615	328.615	0.9417	0.8824	0.9931	1.0087	1.5597	161.61
0.950	344.959	344.958	0.9388	0.8769	0.9964	1.0030	1.6734	88.36
1.000	362.090	362.090	0.9358	0.8713	1.0000	1.0000	1.9332	0.0

Table XI. Parameters Used for the Redlich-Kwong Equation of State with the Lu Modification[a]

component	T_c, K	P_c, MPa	ω	Ω_a	Ω_b	V_c, cm^3/mol
acetone	508.1	4.701	0.3090	0.4423	0.0771	209.0
isopropenylbenzene	654.0	3.404	0.3290	0.4420	0.0749	397.0

[a] The binary interaction constant was assumed to be zero.

that method can reproduce the input pressure values.

Figures 3 and 4 show the activity coefficient values for both the Mixon et al. and Barker (*8*) data reduction methods. The points represent the Mixon et al. results while the curves represent the Barker results. The Barker calculations used the five-constant Redlich-Kister equation to represent G^E and used the same equations of state as the Mixon et al. calculations. Except for the infinite-dilution values at $x_1 = 1.0$, agreement between the two methods was fairly good.

Tables XII and XIII compare the two data reduction methods in terms of the accuracy of the P fits and the values of γ_i^∞ obtained. Seven G^E correlations were tried with the Barker method. Usually, the five-constant Redlich-Kister equation is the one which approaches the Mixon et al. method most closely in the accuracy of the experimental pressure fits, and it has become the "standard" Barker correlation used in the Laboratory. However, the modified Margules equation (also a five-constant equation) of Abbot and Van Ness (*9*) did better than the Redlich-Kister on the isopropylbenzene system and essentially as well on the other system.

All the Barker results agree fairly closely with the Mixon et al. γ_1^∞ values but their γ_2^∞ values are all lower (with the exception of one Margules value).

Further insight concerning the γ_i^∞ values can sometimes be gained by the use of the Gautreaux-Coates equations (*10*) for γ_1^∞ and γ_2^∞. The $(dP/dx_1)_i$ values needed can be obtained from the splined fits or from $P_D/(x_1x_2)$ plots (*11*). The agreement between the two sets of Gautreaux-Coates values for γ_1^∞ is very good and those values agree very well with the Mixon et al. and Barker results. The agreement between the two sets of Gautreaux-Coates values is not so good for γ_2^∞. The $P_D/(x_1x_2)$ plot extrapolations at that end give small intercept values (usually less than 1.0 for these systems) which always cause the inevitable uncertainties in the extrapolated values to be large on a percentage basis. Also, the term in the Gautreaux-Coates equation containing the $(dP/dx_1)_2^\infty$ values is multiplied by the P_1'/P_2' ratio which is high for these systems, and that magnifies the uncertainties in the $(dP/dx_1)_2^\infty$ values. Because of the uncertainties in the graphical extrapolations, the

Table XII. Effect of Calculation Method on γ_i^∞ Values for the Acetone (1) + Isopropylbenzene (2) System and the Virial Equation with the Tsonopoulos Correlation

	accuracy of P fits (max % dev/rmsd)			calcd γ_i^∞ values					
				component 1			component 2		
calculation method	293.15 K	345.15 K	387.15 K	293.15 K	345.15 K	387.15 K	293.15 K	345.15 K	387.15 K
Mixon et al.	0.2/0.1	0.1/0.1	0.1/0.0	2.466	1.995	1.760	2.805	2.633	2.118
Barker:									
absolute Van Laar	4.6/1.4	2.2/0.8	0.7/0.3	2.261	1.909	1.738	2.428	2.183	1.927
Wilson	4.0/1.2	1.8/0.7	0.5/0.2	2.287	1.926	1.749	2.454	2.206	1.937
NRTL	0.9/0.3	0.8/0.3	0.7/0.3	2.432	2.045	1.737	2.585	2.322	1.930
UNIQUAC	4.6/1.4	2.0/0.8	0.6/0.2	2.263	1.919	1.745	2.437	2.198	1.939
modified Margules	0.1/0.1	0.2/0.1	0.4/0.1	2.510	2.016	1.792	2.595	2.833	2.048
Redlich-Kister, three constants	0.8/0.2	1.0/0.4	0.5/0.2	2.432	2.057	1.792	2.564	2.281	1.963
Redlich-Kister, five constants	0.4/0.1	0.8/0.3	0.3/0.1	2.513	2.071	1.784	2.591	2.443	1.999
Gautreaux-Coates:									
splined fits				2.463	1.993	1.759	4.849	3.667	2.399
$P_D/(x_1x_2)$ plots				2.493	1.991	1.750	4.370	2.573	2.306

Table XIII. Effect of Calculation Method on γ_i^∞ Values for the Acetone (1) + Isopropenylbenzene (2) System and the Redlich-Kwong Equation with the Lu Modification

	accuracy of P fits (max % dev/rmsd)			calcd γ_i^∞ values					
				component 1			component 2		
calculation method	295.65 K	331.90 Kq	372.15 K	295.65 K	331.90 K	372.15 K	295.65 K	331.90 K	372.15 K
Mixon et al.	0.2/0.1	0.2/0.1	0.5/0.2	1.822	1.724	1.612	2.344	2.032	1.877
Barker:									
absolute Van Laar	2.6/1.0	2.0/0.7	1.0/0.4	1.751	1.697	1.604	2.017	1.908	1.787
Wilson	2.3/0.9	1.7/0.6	0.9/0.4	1.762	1.705	1.610	2.032	1.918	1.793
NRTL	1.0/0.6	0.2/0.1	0.7/0.2	1.794	1.765	1.639	1.995	1.973	1.819
UNIQUAC	2.5/0.9	1.8/0.6	1.0/0.4	1.756	1.700	1.607	2.022	1.914	1.791
modified Margules	0.6/0.2	0.2/0.1	0.7/0.2	1.862	1.767	1.640	2.414	1.979	2.055
Redlich-Kister, three constants	0.7/0.2	0.4/0.1	0.6/0.2	1.860	1.776	1.643	2.098	1.959	1.812
Redlich-Kister, five constants	0.5/0.2	0.2/0.1	0.6/0.2	1.860	1.758	1.652	2.142	1.966	1.843
Gautreaux-Coates:									
splined fits				1.818	1.723	1.612	7.035	3.304	2.460
$P_D/(x_1x_2)$				1.817	1.740	1.606	6.736	4.868	3.091

splined-fit values probably provide the more reliable Gautreaux–Coates values for these two systems.

The magnitudes of the γ_2^∞ values obtained from the three methods fall in the following order: Barker, Mixon et al., Gautreaux–Coates. The Barker values are related to the G^E correlation constants obtained from a fit of the data points across the entire composition range; hence, the Barker method is often insensitive to any unusual behavior in the P vs. x_1 curves near the end points such as that shown at high x_1 values in Figures 1 and 2. The splined-fit values used by the Mixon et al. method and the Gautreaux–Coates equations are, of course, much more sensitive to the shape of the experimental P curve at the end points. However, the sensitivity often is moderated for the Mixon et al. method by the way that that finite-difference method "reaches" the $x_1 = 0.0$ and 1.0 values. The $G^E = 0$ value at $x_1 = 0$ and at 1.0 plus the two adjacent G^E values at each end are fitted to quadratic equations and the slopes at $x_1 = 0.0$ and 1.0 are obtained from those equations. The slopes sometimes differ appreciably from those given by the splined fits. When that happens, the γ_i^∞ values from the Mixon et al. method are usually lower than those obtained from the Gautreaux–Coates using the splined-fit slopes; i.e., the use of the G^E fits near the end points appears to moderate the values of γ_i^∞ obtained.

It is believed that the Mixon et al. results at high x_1 values are more reliable than the Barker results. Also, any designer using the data should be aware of the relatively high probability that the γ_2^∞ values may be considerably higher than those provided by the Mixon et al. method.

Registry No. Acetone, 67-64-1; isopropylbenzene, 98-82-8; isopropenylbenzene, 98-83-9.

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Heat Capacity of Aqueous Methyldiethanolamine Solutions

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Measurements of the heat capacity of aqueous solutions of methyldiethanolamine (MDEA) containing 23 and 50 wt % amine were made at temperatures of 25, 50, and 75 °C.

Aqueous solutions of methyldiethanolamine (MDEA) are finding increasing use for the selective removal of H_2S from gas mixtures containing hydrogen sulfide and carbon dioxide (*1*). Methyldiethanolamine is a tertiary amine which does not form a carbamate and the rate of reaction with carbon dioxide is slow relative to that with hydrogen sulfide. Little information on the thermophysical properties of MDEA solutions is available. Experimental data for the solubility of H_2S and CO_2 in MDEA solutions have recently been obtained in this laboratory (*2*). There is a need for enthalpies of MDEA solutions for the design of the heat-exchange equipment used in gas treating processes.

Experimental Section

The calorimeter originally devised for the measurement of the enthalpy of solution of CO_2 in alkanolamine solutions (*3*) was used in this work. It consisted of a 1.5-L stainless-steel Dewar closed by a flange sealed by an O-ring. Suspended from the lid were two thermistors, a 240-Ω heater and a cooling coil. The liquid in the calorimeter was stirred with a magnetic stirrer driven by a permanent magnet mounted underneath the Dewar. The calorimeter was immersed in a thermostated oil bath. The temperature of the oil bath was measured by a platinum resistance thermometer calibrated on IPTS-68. The difference in temperature between the calorimeter contents and the oil bath was detected by a set of four Conax TH14 thermistors connected in a differential mode. The thermistors were calibrated by using distilled water with heat capacities taken from Perry (*4*). The methyldiethanolamine was obtained from Aldrich Chemical Co. and had a purity of 97%. The solutions were prepared by weight with distilled water. About 1 L of solution was charged to the calorimeter and allowed to reach the bath temperature. The mass was determined by difference. Electrical energy was added by using a dc power supply in an amount sufficient to cause about a 3 °C temperature rise in 5–6 min. The electrical energy input was determined by using standard resistors and an electrical timer. Cooling water was then circulated through the cooling coil in order to return the contents of the calorimeter to the initial temperature and the experiment was repeated. Four determinations of the heat capacity were made at each temperature for each solution.

Table I. Heat Capacities of MDEA Solutions

	C_p, kJ/(kg °C)	
T, °C	23 wt %	50 wt %
25.0	3.735 ± 0.032	3.380 ± 0.007
50.0	3.773 ± 0.026	3.428 ± 0.013
75.0	3.794 ± 0.014	3.527 ± 0.006

Results and Discussion

The heat capacities were determined at atmospheric pressure for solutions containing 23 and 50 wt % MDEA at temperatures of 25, 50, and 75 °C. The mean values of the heat capacity and the standard deviations of the four determinations are presented in Table I. The data were fitted by least

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