

Excess Gibbs Free Energy, Enthalpy, and Volume and Viscosity of Acetone–Methyl Cellosolve Mixtures

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Isothermal vapor–liquid equilibrium data at 70, 60, and 48.2 °C, and isobaric data at 1 atm pressure are reported for the acetone–methyl cellosolve system. The molar excess enthalpies at 48.2 °C and excess volume at 40 °C are measured in an isothermal phase change calorimeter and a glass dilatometer, respectively. The kinematic viscosity data at 25, 30, 35, 40, and 48.2 °C are obtained by using an Ostwald viscometer. The VLE data are corrected for vapor-phase nonideality and tested for thermodynamic consistency. The kinematic viscosity data are correlated by McAllister and excess function models.

The excess thermodynamic properties are of special interest for alcohol–ketone systems because these systems exhibit nonideality due to association through hydrogen bonding (17). At present there are several different views regarding the attractive interactions between unlike molecules in alcohol–ketone mixtures (15, 16, 21, 22). Our previous study (3b,c) on excess thermodynamic properties of alcohol–ketone systems indicated that the degree of nonideality between methyl cellosolve and ketones increases with higher molecular weight ketones.

Isothermal vapor–liquid equilibrium data at low pressures simplify the study of nonideal behavior of such mixtures because the departure of vapor phase from ideal gas is small. The deviation of viscosity from the rectilinear dependence on volume or mole fraction indicates the possibility of complex formation or the presence of dominant dispersive forces in the mixtures.

The present investigation forms part of a continuing study of excess thermodynamic properties of binary liquid mixtures containing methyl cellosolve as one of the components. No such data have previously been reported in the literature for this system, but data for the acetone–ethyl cellosolve system (25) report similar results.

Experimental Procedures

Materials. Analytical grade acetone and methyl cellosolve (2-methoxyethanol) from British Drug House Co., India, were double distilled in a laboratory distillation column. Table I compares the physical properties of the purified chemicals with the literature values.

Apparatus. The other type of recirculation still (19) was used to collect the equilibrium data. The analytical methods and the operation of the still for isothermal and isobaric conditions are described in the literature (3a,b, 26). These data were measured with air present in the condensate returning to the equilibrium still.

An isothermal phase change calorimeter, similar to one described by Dainton et al. (4), modified by Lakhanpal (12), and calibrated in our laboratories by Kalasy et al. (10), was used for excess enthalpy measurements.

Glass dilatometers, similar to one described in the literature (20), were used for excess volume measurements.

The viscosity of binary mixtures of varying compositions was measured with an Ostwald viscometer, calibrated against the known viscosity of water at different temperatures. The viscometer was thermostated (± 0.02 °C) and the efflux times were measured by visual observations of the meniscus three times for each temperature agreeing to ± 0.5 s. The limits of error in the experimental measurements are estimated as follows:

Table I. Physical Properties of the Chemicals Used

properties	acetone ^a	methyl cellosolve ^a	ref
mol wt	58.08	76.09	
normal bp, °C	56.10 (56.20)	124.50 (124.50)	13
density at 40 °C	0.7674 (0.7682)	0.9462	27
refractive index at 30 °C	1.3560 (1.3566) ^b	1.3991 (1.4004) ^c	13, 27
abs viscosity at 25 °C	0.2869 (0.3075)	1.1917	27
Antoine constants <i>A</i> (58–125 °C)	(7.239 67) <i>B</i> (1279.87) <i>C</i> (237.50)	(8.307 70) (2157.00) (237.16)	5, 8
vapor pressure at 48.2 °C	575.00 (575.31)	39.00 (39.41)	5, 8

^a Values in the parentheses are the literature values. ^b At 25 °C. ^c At 26 °C.

Table II. Isothermal Vapor–Liquid Equilibrium Data for Acetone (1)–Methyl Cellosolve (2)

<i>P</i> , mmHg	<i>x</i> ₁	<i>y</i> ₁	γ ₁	γ ₂	<i>G</i> ^E , cal/mol
At 70 °C					
105	0.0000	0.0000			
144	0.0165	0.2603	2.000	1.027	25.9
170	0.0280	0.3789	2.023	1.029	32.5
193	0.0390	0.4581	1.991	1.029	37.5
225	0.0520	0.5405	2.051	1.030	44.8
314	0.0945	0.6840	1.984	1.030	62.8
352	0.1190	0.7234	1.865	1.037	72.6
445	0.1815	0.7967	1.695	1.032	83.3
506	0.2265	0.8307	1.605	1.031	89.5
662	0.3605	0.8911	1.405	1.042	101.4
At 60 °C					
68	0.0000	0.0000			
291	0.1465	0.7984	1.889	1.045	86.7
311	0.1670	0.8067	1.788	1.044	88.4
370	0.2327	0.8490	1.601	1.050	97.6
407	0.2677	0.8684	1.567	1.052	104.1
492	0.3640	0.8999	1.433	1.110	130.9
602	0.5290	0.9325	1.243	1.230	140.7
648	0.6108	0.9447	1.171	1.310	133.4
At 48.2 °C					
39	0.0000	0.0000			
174	0.1295	0.7909	1.895	1.051	80.6
271	0.2590	0.8838	1.638	1.063	110.6
385	0.4950	0.9361	1.280	1.210	139.6
431	0.6095	0.9531	1.182	1.285	127.6
477	0.7245	0.9649	1.111	1.500	120.2
517	0.8350	0.9780	1.056	1.702	85.2
547	0.9172	0.9885	1.026	1.881	48.6
565	0.9750	0.9962	1.004	2.120	14.4
575	1.0000	1.0000			

enthalpy, ± 0.02 cal/mol; pressure, ± 1 mmHg; temperature, ± 0.1 °C; volume, ± 0.005 mL/mol; viscosity, ± 0.005 cP.

Results and Discussion

The results of isothermal vapor–liquid equilibrium studies are summarized in Table II. The last column contains the values of the molar excess Gibbs free energy.

$$G^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \quad (1)$$

Table III. Isobaric Vapor-Liquid Equilibrium Data for Acetone (1)-Methyl Cellosolve (2) at 1 Atm

$t, ^\circ\text{C}$	x_1	y_1	Z_1	Z_2	γ_1	γ_2
124.5	0.0000	0.0000				
108.5	0.0715	0.4209	1.0925	0.9891	1.403	1.035
96.3	0.1330	0.6263	1.0675	0.9817	1.504	1.093
91.2	0.1568	0.6922	1.0579	0.9769	1.600	1.110
87.0	0.1860	0.7351	1.0520	0.9766	1.600	1.160
84.8	0.2065	0.7583	1.0463	0.9754	1.574	1.182
78.0	0.2832	0.8268	1.0345	0.9717	1.504	1.220
72.3	0.3850	0.8703	1.0251	0.9685	1.374	1.341
66.3	0.5292	0.9090	1.0155	0.9654	1.244	1.580
63.6	0.6090	0.9284	1.0113	0.9639	1.200	1.680
60.0	0.7705	0.9610	1.0058	0.9619	1.100	1.825
58.6	0.8435	0.9733	1.0037	0.9611	1.064	1.952
57.7	0.9020	0.9829	1.0023	0.9606	1.035	2.080
56.4	0.9727	0.9953	1.0004	0.9599	1.014	2.191
65.1	1.0000	1.0000				

Table IV. Excess Molar Enthalpy and Volume for Acetone (1)-Methyl Cellosolve (2)

x_1	H^E , cal/mol	x_1	V^E , mL/mol	x_1	V^E , mL/mol
0.1033	10.5	0.0596	-0.106	0.5616	-0.414
0.2049	36.4	0.1121	-0.175	0.6128	-0.403
0.3137	68.5	0.1591	-0.213	0.6495	-0.393
0.4074	89.2	0.2082	-0.257	0.7067	-0.349
0.5103	96.6	0.2644	-0.291	0.7535	-0.328
0.6090	81.4	0.3119	-0.334	0.8069	-0.272
0.7101	65.6	0.3607	-0.361	0.8571	-0.231
0.8054	49.4	0.4130	-0.376	0.9009	-0.162
0.8999	23.1	0.4688	-0.4041	0.9516	-0.112

Constants in Eq 3				
	C_1	C_2	C_3	RMSD
H^E	372.5	-51.3	-304.1	3.796
V^E	-1.62	-0.25	-0.20	0.029

The isobaric vapor-liquid equilibrium data are reported in Table III. The liquid phase activity coefficients were calculated by using the equation (7)

Table V. Kinematic Viscosity of Acetone (1)-Methyl Cellosolve (2)

x_1	kinematic viscosity, cm^2/s				
	25 $^\circ\text{C}$	30 $^\circ\text{C}$	35 $^\circ\text{C}$	40 $^\circ\text{C}$	48.2 $^\circ\text{C}$
0.0000	1.7045	1.5465	1.3954	1.2595	1.1298
0.0596	1.5145	1.3814	1.2572	1.1545	1.0375
0.1121	1.3699	1.2525	1.1584	1.0649	0.9544
0.1590	1.2515	1.1569	1.0633	0.9842	0.8937
0.2082	1.1432	1.0652	0.9798	0.9119	0.8243
0.2644	1.0515	0.9695	0.9007	0.8397	0.7542
0.3119	0.9726	0.8995	0.8354	0.7794	0.7071
0.3607	0.8999	0.8368	0.7800	0.7308	0.6609
0.4130	0.8025	0.7681	0.7179	0.6769	0.6174
0.4688	0.7565	0.7052	0.6671	0.6244	0.5722
0.5114	0.7032	0.6647	0.6243	0.5850	0.5385
0.5616	0.6564	0.6156	0.5831	0.5457	0.5058
0.6128	0.6078	0.5727	0.5433	0.5109	0.4689
0.6495	0.5743	0.5433	0.5115	0.4851	0.4461
0.7067	0.5305	0.4997	0.4765	0.4527	0.4165
0.7535	0.4945	0.4693	0.4485	0.4277	0.3927
0.8069	0.4611	0.4376	0.4189	0.3986	0.3683
0.8571	0.4332	0.4125	0.3930	0.3751	0.3474
0.9009	0.4093	0.3909	0.3725	0.3564	0.3291
0.9516	0.3863	0.3707	0.3509	0.3349	0.3224
1.0000	0.3656	0.3492	0.3343	0.3188	0.2971

$t, ^\circ\text{C}$	McAllister			excess function			RMSD
	ν_{12}	ν_{21}	RMSD	A''	B''	C''	
25	0.5358	0.9026	0.0023	0.3260	-0.0184	0.1470	0.0032
30	0.5120	0.8348	0.0053	0.3000	-0.0038	0.1646	0.0037
35	0.4809	0.7962	0.0047	0.2450	0.0000	0.1487	0.0057
40	0.4587	0.7514	0.0052	0.2000	0.0100	0.1309	0.0021
48.2	0.4228	0.6776	0.0032	0.1830	0.0250	0.2625	0.0052

$$\gamma_i = \frac{\pi y_i}{P_i^\circ x_i} \exp \left[\frac{(P_i^\circ - \pi)(V_i - \beta_i)}{RT} \right] \quad (2)$$

The exponential term in eq 2 represents the vapor phase nonideality correction (Z_i) in calculating the activity coefficients, the values of which are computed for each data point from the vapor pressure and the second virial coefficient of pure components. The pure component vapor pressures were calculated over the temperature range of the binary by the Antoine (1) equation through the constants reported in Table I. The gas-phase second virial coefficients for acetone and methyl cellosolve were calculated by using Black's (2) and O'Connell's (18) correlations, respectively, with the parameters reported by Prausnitz et al. (24). Goldhammer's correlation (6) estimated the liquid molar volumes for both the components at equilibrium temperatures.

Experimental values of molar excess enthalpy and molar excess volume are reported in Table IV. The method of least squares was used to fit the results of the excess properties with a Redlich-Kister type equation:

$$X^E = x_1 x_2 \sum_{q=1}^n C_q (1 - 2x_1)^{q-1} \quad (3)$$

The coefficients in eq 3 along with the root-mean-square deviations of the estimate are reported in Table IV. The data are presented graphically in Figure 1.

The experimental data on viscosity of binary mixtures are reported in Table V. The data were correlated by McAllister (14) and excess function models (17).

The isobaric VLE data were tested for thermodynamic consistency through the Gibbs-Duhem equation written in the form

$$\int_0^1 \ln \gamma_1 / \gamma_2 dx_1 = \int_{x_1=0}^{x_1=1} H^E / RT^2 dT \quad (4)$$

The right-hand term of eq 4 was evaluated by using heats of mixing at 48.2 $^\circ\text{C}$ and the temperature-composition data from

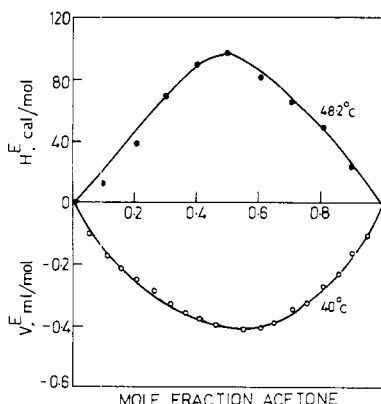


Figure 1. Molar excess enthalpy (48.2 °C) and volume (40 °C) for acetone (1)-methyl cellosolve (2).

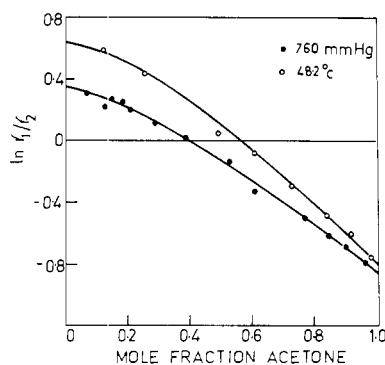


Figure 2. Thermodynamic consistency by Herington's criteria.

VLE studies and was found to be -0.1285 . The left-hand side term on graphical integration was equal to -0.1310 , indicating the consistency of the equilibrium data.

The isothermal VLE data at $48.2\text{ }^\circ\text{C}$ were tested for thermodynamic consistency through Herington's criteria (9). From Figure 2 the consistency index (23) was found to be 0.035 , which is very close to the suggested limit, indicating the consistency of the data.

The kinematic viscosity of the pure components were fitted in the equation

$$\ln \nu = A' + B'/T \quad (5)$$

where A' and B' are constants and T is absolute temperature, K. These constants over the temperature range of $25\text{--}48.2\text{ }^\circ\text{C}$ are as follows: acetone, $A' = -3.8506$, $10^{-2}B' = 8.4848$; methyl cellosolve $A' = -5.3870$, $10^{-2}B' = 17.6470$.

Conclusion

The system acetone-methyl cellosolve consists of polar and associative ketone and polar alcohol. Raoult's law deviations are positive. This is a wide boiling system for which no correlating equation was found to be suitable to represent the data satisfactorily. The excess enthalpy of mixing is small and positive indicating weak interactions between the molecular species. Our previous study (3b, c) indicated that the degree of nonideality between alcohol-ketone molecules increases with increase in the molecular weight of ketone. This is judged from the activity coefficient data and the excess enthalpy data. The rise in the temperature will disrupt the alcohol-ketone association which can be observed from the decrease in the activation energy ν_{12} and ν_{21} with increase in temperature from Table V.

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Glossary

- A, B, C constants in Antoine vapor-pressure equation
 A', B' constants in eq 5
 A'', B'', C'' excess function model constants
 C_1, C_2, C_3 constants in representing the excess properties by eq 3
 G^E molar excess Gibbs free energy, cal/mol
 H^E molar excess enthalpy, cal/mol
 P° vapor pressure of pure components, mmHg
 P system pressure, mmHg
 x_i mole fraction of component i in liquid phase
 y_i mole fraction of component i in vapor phase
 X^E molar excess property
 Z_1, Z_2 vapor phase nonideality corrections, exponential term in eq 2
 RMSD root-mean-square deviation = $[\sum(\gamma_{1\text{expt}} - \gamma_{1\text{calcd}})^2/N]^{1/2}$
 N number of data points
- Greek Letters**
- β gas phase second virial coefficient of pure component, mL/mol
 γ activity coefficient of component in liquid phase
 π total pressure, mmHg
 ν kinematic viscosity, cm^2/s
 ν_{12}, ν_{21} parameters in McAllister model
- Subscripts**
- 1 more volatile component
 2 less volatile component
 i component i
 calcd calculated

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