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Vapor-Liquid Equilibria of Acetylacetone-Organic Solvent Systems

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The vapor-liquid equilibria of pure acetylacetone and acetylacetone-organic solvent mixtures, viz., acetylacetone-cyclohexane, -carbon tetrachloride, -toluene, -benzene, and -chloroform, were measured at 25 °C over the whole composition range. The densities of the liquid mixtures were measured at 25 °C. From these measurements were calculated the thermodynamic functions including the activity coefficient and the excess free energy of mixing. The activity coefficients for keto and enol tautomers of acetylacetone were estimated separately by the aid of Wilson's equation. The distribution coefficients of acetylacetone between aqueous and organic solvent phases, as defined in liquid-liquid extraction, were predicted and compared with those determined experimentally. A good agreement was clearly observed except in the chloroform system.

Introduction

Acetylacetone (2,4-pentanedione) and related compounds are capable of reacting with many metal cations to form extractable complexes, and the study of solvent-extraction systems involving these compounds is now very extensive, but the systematic progress of solvent-extraction chemistry is hampered by a lack of knowledge of the thermodynamic properties of these compounds themselves.

Published data on the vapor pressure of acetylacetone are meager and not consistent; the enthalpies of vaporization derived from these vary between 27 and 48 kJ mol^{-1} (*1-4*). It seems probable that the discrepancies in these published data were mainly due to fluctuations in measurements made in an incomplete equilibrium state. Acetylacetone consists of two tautomers; i.e., enol and keto forms, and the rate of tautomerization is quite slow and susceptible to the environmental solvent (*5*, *6*).

The present study was undertaken to obtain the thermodynamic quantities of acetylacetone in cyclohexane, carbon tetrachloride, toluene, benzene, and chloroform. We have measured the vapor pressure and the density, and the tautomerization in these systems was also examined. A reliable measurement of vapor pressures of systems containing acetylacetone is very difficult, because acetylacetone is a very active compound and consists of two tautomers, and the rate of tautomerization is quite slow. We constructed a new apparatus for static vapor-liquid equilibrium measurement, by which the accurate measurement of the vapor pressure of active species such as acetylacetone can be attained (*7*). However, the vapor pressure thus obtained is of the mixture of two tautomers of acetylacetone. The keto and enol tautomers of acetylacetone are not homologous molecules. There is a distinguishable difference in the intermolecular forces of like-like and like-unlike molecule pairs among these tautomers, and it is practically impossible to isolate chemically each tautomer and to determine independently intrinsic thermodynamic quantities for each species.

In this study, the thermodynamic quantity for each tautomer was estimated with the aid of Wilson's equation, and the reliability of these estimated values was examined. Finally, the distribution coefficients of these species in different organic solvent systems were estimated and compared with those determined experimentally.

Experimental Section

Materials. G. R. grade acetylacetone (Wako Chemical Industries Ltd.) was washed with aqueous ammonia solution, dried over anhydrous sodium sulfate, and then fractionally distilled. Values of the density, the refractive index (μ_D), and the vapor pressure, determined for this material at 25 °C, were 0.9684 g cm^{-3}, 1.4511, and 9.69 torr, respectively.

G. R. grade benzene (Wako Chemical Industries Ltd.) was treated with concentrated sulfuric acid until thiophene free. After repeated water washes, it was dried first with calcium chloride and then with metallic sodium and fractionally distilled. Values of the density, the refractive index, and the vapor pressure at 25 °C were 0.8736 g cm^{-3}, 1.4979, and 95.26 torr, respectively.

G. R. grade toluene was purified by the same method as benzene purification. Values of the density and the vapor pressure at 25 °C were 0.8621 g cm^{-3} and 28.50 torr, respectively.

G. R. grade cyclohexane (Wako Chemical Industries Ltd.) was nitrated with a mixture of nitric acid and sulfuric acid at 20-25 °C for 6 h, washed several times with concentrated sulfuric acid, potassium permanganate solution, water, sodium hydroxide, and water successively, dried over calcium chloride, and fractionally distilled. Values of the density, the refractive index, and the vapor pressure at 25 °C were 0.7735 g cm^{-3}, 1.4237, and 97.68 torr, respectively.

Carbon tetrachloride was washed with sodium hydroxide solution in aqueous alcohol at 50-60 °C for 0.5 h. This treatment was repeated several times, and the carbon tetrachloride was washed with water and concentrated sulfuric acid until no color was detected. After being washed with water, it was dried over calcium chloride and then fractionally distilled. Values of the density, the refractive index, and the vapor pressure at 25 °C were 1.5844 g cm^{-3}, 1.4575, and 114.0 torr, respectively.

G. R. grade chloroform (Wako Chemical Industries Ltd.) was treated with dilute sodium hydroxide solution, washed with water, dried over calcium chloride, and fractionally distilled. Values of the density and the vapor pressure at 25 °C were 1.4793 g cm^{-3} and 196.05 torr, respectively.

To avoid decomposition by light, we conducted all treatments for the purification of carbon tetrachloride and chloroform under a red lamp and by using a distillation apparatus covered with aluminum foil. The gas-chromatographic analysis of the purified solvents does not show any significant peaks due to impurities.

Vapor-Pressure Measurements. The vapor-pressure assembly described in a previous paper (*7*) was employed for the acetylacetone-organic solvent systems. The apparatus is a completely static one and is appropriate to measure the vapor pressure of active materials at a given temperature within ±0.001 °C. To test the reliability of this assembly, we measured the vapor pressure of the benzene-cyclohexane system and compared it with the literature value. The precision of the new assembly was within ±1.5%; this is equal to, or better

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Table I. Vapor Pressure of Acetylacetone

temp, °C	P_{measd}, torr	P_{calcd},[a] torr	temp, °C	P_{measd}, torr	P_{calcd},[a] torr
22.02	8.29	8.23	34.95	16.60	16.58
25.01	9.75	9.78	40.01	21.38	21.41
30.37	13.07	13.05			

[a] Calculated from eq 1.

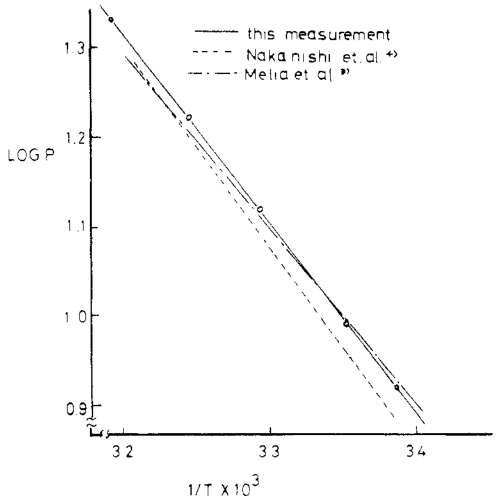

Figure 1. Vapor pressure of acetylacetone as a function of temperature.

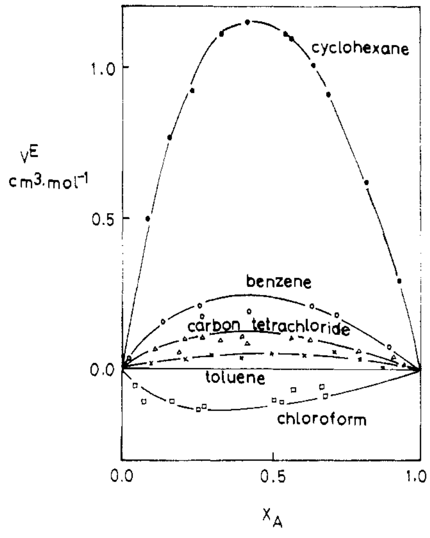

Figure 2. Excess volume of acetylacetone-organic solvent systems at 25 °C.

than, that of Scatchard's values for the same binary solvent system (*7*, *8*). In the present system involving acetylacetone, a steady pressure reading was usually obtained less than 10 h after each change in the composition or alternation of the system of acetylacetone–organic solvent, but, to avoid any error due to an incomplete equilibrium in the tautomerization of acetylacetone, we made all pressure readings ~20 h after each change of composition and system.

Density Measurements. The densities of the pure liquids and the mixtures were determined by Lipkin-Devison-type pycnometers with capacities of ca. 4, 2.5, and 1.5 cm³. All measurements were made at 25 °C in a water thermostat; the temperature was controlled within ±0.02 °C. A volume reading was made after placing all of the mixtures for over 10 h in a thermostat to attain the equilibrium of tautomerization. Density measurements were also employed for the analysis of the compositions of the vapor and liquid phases. The error in the mole fraction is less than ±0.001.

Determination of Acetylacetone Tautomer. The keto fraction of acetylacetone was determined from the NMR signal of the methyl protons of acetylacetone at 25 ± 0.5 °C. The magnetic resonance spectra were taken on a JEOL JNM PS-100. To make sure of the keto-enol equilibrium of acetylacetone, we stored all mixtures for a sufficient time in the water thermostat controlled at 25 °C.

Results

Vapor Pressure of Acetylacetone. The vapor pressure of pure acetylacetone was measured at five different temperatures. Results for the vapor pressure of acetylacetone are given in Table I and Figure 1. The vapor pressure of acetylacetone over the temperature range 22.02–40.01 °C is represented by eq 1. The constants in this equation were

$$\log P(\text{torr}) = 8.09857 - 2119.52/T(\text{K}) \qquad (1)$$

determined by the least-squares method. A good linear correlation is clearly observed, and the deviation of the experimental value from this straight line is not greater than 0.02 torr, which is comparable with a reading error of the mercury manometer. Literature data are also given in Figure 1, but the deviation is greater than 0.2 torr and it might be suspected that these experiments were made in an incomplete equilibrium state. Based on the present data, the heat of vaporization of acetylacetone was calculated as 40.58 kJ mol⁻¹; this value can be compared with the value of 41.77 ± 0.05 kJ mol⁻¹ obtained calorimetrically by Irving and Wadso (*9*).

Vapor Pressure of Acetylacetone–Organic Solvent Systems. Vapor pressures of acetylacetone–benzene, acetylacetone–cyclohexane, acetylacetone–carbon tetrachloride, acetylacetone–toluene, and acetylacetone–chloroform systems were measured at 25.00 °C.

In Table II are given the vapor pressure, P, and the composition expressed as the mole fraction of acetylacetone in the liquid and vapor phases, X_A and Y_A, respectively.

Excess Volume of Acetylacetone–Organic Solvent Systems. The densities of the five systems studied are summarized in Table III. As the density of pure acetylacetone is measured to be 0.9684 g cm⁻³, the apparent molar volume of acetylacetone is calculated as 103.4 cm³ mol⁻¹. The excess volume calculated from the density data is also given in the same table and is plotted as a function of mole fraction of acetylacetone in Figure 2.

Keto–Enol Equilibrium of Acetylacetone–Organic Solvent Systems. The effect of solvents on the keto–enol equilibrium has also been examined for acetylacetone in cyclohexane, carbon tetrachloride, toluene, benzene, and chloroform. The keto fractions determined by NMR measurement are summarized in Table IV. These keto fractions are fitted by least squares to the following type of equation:

$$X_K = AX^2 + BX + C \qquad (2)$$

where X_K and X are the mole fractions of the keto species and of acetylacetone, respectively. The coefficients A, B, and C are given in Table IV.

To examine the temperature dependence of the tautomerization, we measured the keto fractions of acetylacetone at different temperatures in the range 10–40 °C. These values are shown in Table V. The values of $\log (X_K/X_E)$ vs. $1/T$ are plotted in Figure 3, where X_K and X_E are the mole fractions of the keto and enol forms of acetylacetone in equilibrium, respectively. The equilibrium constants, X_K/X_E, are fitted to eq

$$\log X_K/X_E = -477.9/T(\text{K}) + 0.9578 \qquad (3)$$

3 over the temperature range 10–40 °C. The value 9.150 kJ mol⁻¹ calculated for the ketonization enthalpy is smaller than

Table II. Comparison of Experimental and Calculated Values for the Vapor-Liquid Equilibria of Acetylacetone (A)-Organic Solvent (B) Systems at 25 °C

x_A	y_A	$y_{A,calcd}$[a]	y_E/y_A[b]	P, torr	P_{calcd},[c] torr	γ_E	γ_K	γ_S	G^E,[a] J mol^{-1}
(a) Acetylacetone–Cyclohexane									
0.0	0.0	0.0		97.68	97.68	7.001	64.047	1.000	0.0
0.092	0.044	0.041	0.941	93.70	95.16	3.843	14.980	1.029	385.3
0.124	0.052	0.048	0.946	92.82	94.22	3.308	11.130	1.048	489.2
0.299	0.074	0.068	0.950	88.57	89.63	1.889	4.068	1.220	857.7
0.373	0.080	0.073	0.949	86.65	87.59	1.617	3.121	1.325	930.9
0.469	0.087	0.081	0.947	84.06	84.40	1.382	2.382	1.496	964.8
0.517	0.091	0.085	0.946	81.76	82.42	1.297	2.130	1.598	957.8
0.582	0.098	0.092	0.943	79.31	79.14	1.206	1.865	1.760	924.2
0.600	0.101	0.094	0.943	77.89	78.07	1.185	1.804	1.810	910.0
0.702	0.117	0.111	0.939	73.67	70.35	1.091	1.529	2.148	791.6
0.809	0.152	0.146	0.935	59.08	57.60	1.033	1.333	2.638	597.7
0.915	0.255	0.247	0.931	35.80	36.79	1.007	1.200	3.336	334.4
1.0	1.0	1.0	0.926	9.76	9.76	1.009	1.123	4.161	71.5
(b) Acetylacetone–Carbon Tetrachloride									
0.0	0.0	0.0		114.00	114.00	2.065	3.353	1.000	0.0
0.143	0.020	0.024	0.972	103.29	102.08	1.582	2.386	1.020	213.2
0.291	0.041	0.044	0.964	92.42	90.87	1.314	1.855	1.075	342.5
0.377	0.054	0.057	0.959	85.49	84.24	1.215	1.658	1.119	381.7
0.544	0.084	0.087	0.950	70.57	69.97	1.095	1.405	1.229	393.2
0.754	0.163	0.163	0.939	47.08	47.28	1.024	1.226	1.411	302.9
0.838	0.236	0.233	0.935	35.80	36.06	1.012	1.181	1.499	238.1
1.0	1.0	1.0	0.926	9.76	9.76	1.009	1.123	1.693	71.5
(c) Acetylacetone–Toluene									
0.0	0.0	0.0		28.50	28.50	1.580	3.899	1.000	0.0
0.131	0.063	0.069	0.941	26.86	26.93	1.357	2.154	1.013	143.3
0.235	0.094	0.118	0.949	25.77	25.60	1.251	1.660	1.036	215.9
0.361	0.163	0.179	0.952	23.87	23.84	1.162	1.364	1.075	265.7
0.497	0.242	0.253	0.951	21.59	21.67	1.097	1.205	1.129	279.9
0.570	0.291	0.301	0.949	20.31	20.35	1.072	1.157	1.162	272.7
0.970	0.879	0.890	0.927	10.72	10.66	1.011	1.116	1.371	93.0
1.0	1.0	1.0	0.926	9.76	9.76	1.009	1.123	1.388	71.5
(d) Acetylacetone–Benzene									
0.0	0.0	0.0		95.26	95.26	1.416	3.160	1.00	0.0
0.137	0.021	0.021	0.939	84.59	84.93	1.238	1.973	1.012	115.4
0.339	0.056	0.054	0.944	70.01	70.20	1.109	1.410	1.054	199.2
0.464	0.082	0.082	0.943	59.96	60.57	1.065	1.265	1.089	213.6
0.614	0.131	0.131	0.940	48.70	48.05	1.034	1.175	1.135	202.1
0.700	0.173	0.175	0.937	40.63	40.30	1.023	1.147	1.163	184.0
0.787	0.246	0.245	0.934	32.05	32.00	1.016	1.131	1.191	158.6
0.895	0.431	0.418	0.929	20.78	21.05	1.011	1.121	1.226	118.7
1.0	1.0	1.0	0.926	9.76	9.76	1.009	1.123	1.259	71.5
(e) Acetylacetone–Chloroform									
0.0	0.0	0.0		196.05	196.05	0.604	0.605	1.0	0.0
0.134	0.003	0.006	0.945	171.84	168.88	0.698	0.737	0.989	−139.9
0.213	0.008	0.010	0.942	155.75	151.84	0.750	0.811	0.974	−197.5
0.278	0.013	0.016	0.940	140.97	137.63	0.789	0.867	0.957	−231.8
0.363	0.022	0.025	0.937	120.54	119.14	0.837	0.934	0.930	−259.5
0.453	0.038	0.039	0.935	100.11	100.06	0.881	0.995	0.896	−268.6
0.491	0.049	0.047	0.934	91.29	92.25	0.897	1.017	0.881	−266.4
0.648	0.107	0.098	0.930	61.91	62.06	0.954	1.089	0.812	−221.3
0.813	0.261	0.226	0.928	33.92	34.72	0.992	1.125	0.733	−115.2
0.907	0.459	0.413	0.926	21.85	21.36	1.004	1.129	0.688	−29.6
1.0	1.0	1.0	0.926	9.76	9.76	1.009	1.123	0.643	71.5

[a] Calculated from eq 14. [b] Calculated from eq 12. [c] Calculated from eq 13. [d] Calculated from eq 15.

the literature value of 11.31 ± 0.41 kJ mol^{-1} obtained by Reevs (*10*).

Discussion

The keto and enol tautomers of acetylacetone cannot be isolated experimentally. We have attempted to estimate the vapor pressure of keto and enol forms of acetylacetone.

If one assumes that the vapor of acetylacetone behaves as an ideal gas, the vapor pressure of acetylacetone is given by eq 4, where P_A, P^0, X, and γ represent the total vapor pressure of acetylacetone, the vapor pressure of the tautomer of acetylacetone, the mole fraction, and the activity coefficient, and subscripts E and K designate the enol form and the keto form, respectively. The vapor pressure of acetylacetone is represented by eq 1, and X_E and X_K are represented by eq 3, as functions of temperature.

$$P_A = P_E^0 X_E \gamma_E + P_K^0 X_K \gamma_K \quad (4)$$

The activity coefficients are expressed by Wilson's equation as follows (*11*):

$$\ln \gamma_i = 1 - \ln \left[\sum_{j=1}^{n} x_j \Lambda_{ij}\right] - \sum_{k=1}^{n} \left[x_k \Lambda_{ki} / \left(\sum_{j=1}^{n} x_j \Lambda_{kj}\right)\right] \quad (5)$$

Here

$$\Lambda_{ij} = \frac{V_j}{V_i} \exp\left[-\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right] \quad (6)$$

Table III. Density and Excess Volume at 25.0 °C

mole fraction of acetylacetone	density, g cm^{-3}	excess vol, cm^3 mol^{-1}	mole fraction of acetylacetone	density, g cm^{-3}	excess vol, cm^3 mol^{-1}
(a) Acetylacetone–Cyclohexane					
0.0	0.7735	0.0	0.5626	0.8717	1.0917
0.0848	0.7857	0.4926	0.6393	0.8873	1.0082
0.1574	0.7972	0.7669	0.6899	0.8981	0.9026
0.2324	0.8101	0.9196	0.8146	0.9253	0.6138
0.3314	0.8272	1.1264	0.9279	0.9510	0.2912
0.4182	0.8435	1.1494	1.0	0.9684	0.0
0.5487	0.8689	1.1054			
(b) Acetylacetone–Carbon Tetrachloride					
0.0	1.5844	0.0	0.4189	1.3158	0.0832
0.1098	1.5119	0.0640	0.5625	1.2272	0.1003
0.1897	1.4606	0.0595	0.6263	1.1885	0.0954
0.2064	1.4493	0.1022	0.7901	1.0908	0.0563
0.2668	1.4109	0.1033	0.9100	1.0204	0.0356
0.2930	1.3940	0.1276	0.9380	1.0043	0.0106
0.3320	1.3699	0.0957	1.0	0.9684	0.0
0.4040	1.3248	0.1031			
(c) Acetylacetone–Toluene					
0.0	0.8621	0.0	0.4993	0.9139	0.0455
0.0946	0.8717	0.0168	0.6074	0.9254	0.0425
0.2064	0.8832	0.0291	0.7133	0.9367	0.0540
0.2939	0.8922	0.0468	0.7908	0.9452	0.0320
0.3948	0.9029	0.0336	1.0	0.9684	0.0
(d) Acetylacetone–Benzene					
0.0	0.8736	0.0	0.4247	0.9155	0.1846
0.0204	0.8755	0.0317	0.6325	0.9347	0.2042
0.1342	0.8865	0.1535	0.7159	0.9425	0.1774
0.2588	0.8989	0.2045	0.8865	0.9583	0.0641
0.2683	0.9001	0.1797	1.0	0.9684	0.0
(e) Acetylacetone–Chloroform					
0.0	1.4793	0.0	0.5329	1.1774	−0.1142
0.0441	1.4523	−0.0618	0.5683	1.1595	−0.0708
0.0715	1.4354	−0.1104	0.6656	1.1131	−0.0626
0.1647	1.3784	−0.1091	0.0680	1.1086	−0.0968
0.2580	1.3240	−0.1384	0.8753	1.0195	−0.0090
0.2719	1.3161	−0.1285	1.0	0.9684	0.0
0.5096	1.1890	−0.1070			

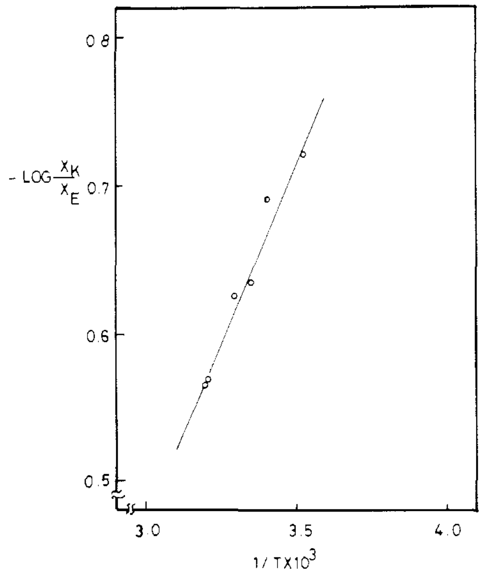

Figure 3. Variation in concentration of tautomeric forms in pure acetylacetone with temperature.

where the subscripts represent components in the mixture and *V* is the molar volume of the pure component. The λs are the terms corresponding to the energies of interaction between the molecules designated in the subscripts; λ_{ij} is equal to λ_{ji}, and $\lambda_{ij} - \lambda_{ii}$ is regarded as a constant without serious error, at least over modest temperature intervals. The exact values of the molar volumes for the keto and enol forms of acetylacetone cannot be determined directly. The molar volumes of the keto and enol forms of acetylacetone were estimated on the basis of the additivity rule of the atomic volumes (*12*). The molar volumes of 118.4 cm^3 mol^{-1} for the keto tautomer and 108.0 cm^3 mol^{-1} for the enol tautomer are obtained, but these values correspond to those at the boiling point.

Table IV. Solvent Effect on the Keto-Enol Equilibrium of Acetylacetone-Organic Solvent Systems at 25 °C

X_1	keto, %	X_1	keto, %
(a) Acetylacetone–Cyclohexane			
0.300	6.8	0.774	13.5
0.398	8.7	1.0	18.8
0.555	10.6		
(b) Acetylacetone–Carbon Tetrachloride			
0.139	5.3	0.512	11.2
0.226	6.4	0.621	11.7
0.408	10.1	0.734	13.2
0.428	10.6	0.825	15.8
0.502	11.0	1.0	18.8
(c) Acetylacetone–Toluene			
0.224	11.2	0.722	14.7
0.399	12.2	0.735	15.4
0.586	13.6	1.0	18.8
(d) Acetylacetone–Benzene			
0.080	11.1	0.546	14.4
0.248	11.9	0.701	16.4
0.290	12.8	0.707	15.6
0.481	13.7	1.0	18.8
(e) Acetylacetone–Chloroform			
0.265	15.5	0.614	17.4
0.377	15.9	0.717	17.8
0.419	16.2	0.723	17.1
0.441	16.3	1.0	18.8
0.473	16.1		

systems	A^a	B^a	C^a
a	4.645	9.326	3.884
b	0.9135	13.82	3.635
c	7.805	0.1822	10.82
d	2.610	5.702	10.58
e	−0.2220	4.630	14.21

[a] Coefficient in eq 2.

Table V. Keto Fraction of Pure Acetylacetone as a Function of Temperature

temp, °C	keto, %	X_K/X_E	temp, °C	keto, %	X_K/X_E
10	16.0	0.1905	30	19.2	0.2376
20	16.9	0.2034	39	21.2	0.2690
25	18.8	0.2315	40	21.4	0.2723

The apparent molar volume and the enol and keto fractions of acetylacetone have been determined in the present work as 103.4 cm^3 mol^{-1}, 81.2%, and 18.8%, respectively. If one assumes that the molar volume ratio of keto to enol tautomers at the boiling point is held constant regardless of temperature, the molar volumes of the enol and keto tautomers at 25 °C can be estimated separately as 101.59 and 110.99 cm^3 mol^{-1}, respectively. The vapor pressures of the enol and keto tautomers are represented by the following type of equation:

$$\log P_i^0 = A_i - B_i/T \tag{7}$$

where A_i and B_i are constants.

P_A in eq 4 can be rearranged by combination with eq 5–7. In the application of these equations to the present systems, X_E, X_K, V_E, and V_K are known, but A_E, B_E, A_K, B_K, $\lambda_{EK} - \lambda_{EE}$, and $\lambda_{KE} - \lambda_{KK}$ are not. These numerical constants are esti-

Table VI. Fitted Wilson Parameters[a] in the System of Acetylacetone and Organic Solvents

solvents	$\lambda_{SE} - \lambda_{SS}$	$\lambda_{SE} - \lambda_{EE}$	$\lambda_{SK} - \lambda_{SS}$	$\lambda_{SK} - \lambda_{KK}$
cyclohexane	1100	4000	2800	8600
carbon tetrachloride	0.0	1800	400	2600
toluene	50	1090	−1630	5770
benzene	−50	940	−1170	4770
chloroform	−220	−890	−1020	630

[a] In units of J mol^{-1}.

mated by computer fitting so as to fulfill the measured total pressure P_A. The results are summarized as follows:

$$\lambda_{EK} - \lambda_{EE} = -420 \text{ J mol}^{-1} \tag{8}$$

$$\lambda_{KE} - \lambda_{KK} = 1030 \text{ J mol}^{-1} \tag{9}$$

$$\log P_E^0(\text{torr}) = 8.2388 - 2146.16/T(\text{K}) \tag{10}$$

$$\log P_K^0(\text{torr}) = 8.8513 - 2477.3/T(\text{K}) \tag{11}$$

By using these numerical constants, we can predict the mole fraction of the enol tautomer in the vapor phase and the boiling point of the enol tautomer of acetylacetone. If one assumes that the vapor of acetylacetone is an ideal gas, the mole fraction of the enol tautomer in the vapor phase is given by eq 12, where Y is the mole fraction in the vapor phase.

$$\frac{Y_E}{Y_K + Y_E} = \frac{P_E^0 X_E \gamma_E}{P_E^0 X_E \gamma_E + P_K^0 X_K \gamma_K} \tag{12}$$

The mole fraction, Y_E, at 25 °C is calculated as 0.923; this is very close to the value estimated experimentally by Strohmeier, 0.929 (*13*). From eq 10 and 11 the boiling points of the enol and keto tautomers are calculated as 127.4 and 141.3 °C, respectively, and the calculated boiling point for the enol tautomer is close to the boiling point roughly estimated by Irving and Wadso, ~129 °C (*9*). Accordingly, these numerical constants, estimated as summarized in eq 8–11, are reasonable ones. From eq 10 and 11 the enthalpies of vaporization of the enol and keto tautomers are estimated as 41.1 and 47.4 kJ mol^{-1}, respectively. The Wilson energy parameters (λs) may not have a precise significance but can be taken as a measure of the intermolecular force between species in solution, and qualitatively the relative values given in eq 8 and 9 suggest the sequence of intermolecular interaction between the tautomers of acetylacetone as follows: enol–enol < enol–keto < keto–keto.

One of the advantages of Wilson's equation is that it may be extended to as many components as desired without any additional assumption and without introducing any constants other than those obtained from binary data. The same treatment described above has been extended to the acetylacetone–organic solvent systems.

The vapor pressure of acetylacetone–organic solvent systems is given by eq 13, where P, P_S^0, and X_S are the total

$$P = P_E^0 X_E \gamma_E + P_K^0 X_K \gamma_K + P_S^0 X_S \gamma_S \tag{13}$$

vapor pressure of the system, the vapor pressure of the pure organic solvent, and the mole fraction of the organic solvent, respectively. The activity coefficients of the components, γ_E, γ_K, and γ_S, are represented by eq 5.

Since P, P_S^0, X_S, X_E, and X_K can be measured and P_E^0 and P_K^0 are represented by eq 7, 10, and 11, the most appropriate λ parameters to fit P in relation to eq 5 can be estimated by computer fitting techniques and are summarized in Table VI.

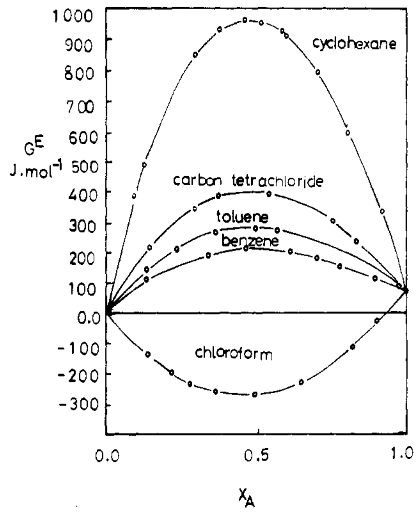

Figure 4. Excess Gibbs free energy of acetylacetone–organic solvent systems at 25 °C.

The activity coefficients of the species have been calculated and are summarized in Table II. It is clear that, in all of the solvent systems except the chloroform system, the activity coefficients of the keto and enol tautomers are larger than unity and, furthermore, the activity coefficient of the keto tautomer is larger than that of the enol tautomer. The ratio γ_B/γ_K decreases with decreasing concentration of acetylacetone. In the acetylacetone–chloroform system, on the other hand, the activity coefficients of the keto and enol forms are less than unity.

To examine the reliability of these approximations, one can calculate the mole fraction of acetylacetone in the vapor phase and compare it with the experimental value. The mole fraction of acetylacetone in the vapor phase, Y_A, is given by eq 14,

$$Y_A = \frac{Y_E + Y_K}{Y_E + Y_K + Y_S} = \frac{P_E^0 X_E \gamma_E + P_K^0 X_K \gamma_K}{P_E^0 X_E \gamma_E + P_K^0 X_K \gamma_K + P_S^0 X_S \gamma_S} \tag{14}$$

assuming an ideal gas behavior for all vapor species. In Table II is a comparison of the values calculated by eq 14 with the observed ones. Good coincidence is observed. This means that the estimated parameters are reasonable and that Wilson's equation can be applied to a system which includes a chemical transformation such as tautomerization.

The enol fractions of acetylacetone in the vapor phase in acetylacetone–organic solvent systems are also calculated and given in Table II as Y_E/Y_A ($= Y_E/(Y_E + Y_K)$). A nearly constant value of Y_E/Y_A is obtained in every system in which the vapor phase is equilibrated with the liquid phase containing a wide concentration range of acetylacetone, and practically no solvent effect is observed in the vapor phases.

The excess Gibbs free energy, G^E, is given in eq 15. The

$$G^E = RT\sum X_i \ln \gamma_i \tag{15}$$

values of the excess Gibbs free energy function of acetylacetone–organic solvent systems at 25 °C are also given in Table II and are plotted against the mole fraction in Figure 4. The excess Gibbs free energies of the acetylacetone–cyclohexane system show large positive values, and the other systems, except the chloroform system, also show positive ones. A small positive value observed at $X_A = 1.0$ may be attributed to a mixing of keto and enol tautomers of acetylacetone. The negative excess Gibbs free energies of the acetylacetone–chloroform system suggest the presence of an intermolecular force between acetylacetone and chloroform, and this interaction has been observed in an NMR study (*14*).

Recalling the main objective of the present work, one must try to compare the distribution coefficients of acetylacetone

Table VII. Comparison of Distribution Coefficients of Acetylacetone

organic solvent	K_{org}	D_A[a]	$K^x{}_{\mathrm{DE}}$[b]	$K^x{}_{\mathrm{DE}}/K^x{}_{\mathrm{DE,CCl_4}}$[c]	$1/\gamma_E{}^{\infty}$[d]	$K^x{}_{\mathrm{DK}}$[b]	$K^x{}_{\mathrm{DK}}/K^x{}_{\mathrm{DK,CCl_4}}$[c]	$1/\gamma_K{}^{\infty}$[d]
cyclohexane	0.0404	1.03[e]	35.19	0.35	0.29	0.29	0.28	0.052
carbon tetrachloride	0.0377	3.31[e]	101.13	1.00	1.00	1.02	1.00	1.00
		3.18[f]	97.28	1.00		0.76	1.00	
toluene	0.121	4.57[e]	142.27	1.41	1.31	3.53	3.46	0.860
		4.18[f]	130.09	1.34		3.23	4.25	
benzene	0.118	5.93[e]	155.04	1.53	1.46	3.72	3.65	1.02
		5.45[f]	142.37	1.46		3.41	4.49	
chloroform	0.166	23.80[e]	538.56	5.33	3.42	18.19	17.83	5.54
		23.28[f]	526.73	5.41		17.80	23.42	

[a] Distribution coefficient of acetylacetone in aqueous–organic solvent system. Reference *14* and *17*. [b] Distribution coefficient of the tautomer. [c] Shown as a relative value in which the value in carbon tetrachloride is arbitrarily chosen as unity. [d] Relative activity coefficient of the tautomer; see text. [e] Reference *14*. [f] Reference *17*.

predicted from the thermodynamic activity coefficients with those determined experimentally. When a substance B is added to a system of two liquid phases, consisting of two immiscible or slightly miscible liquids, the activities of B in both phases are equal in the distribution equilibrium. The distribution between an organic phase and an aqueous phase is shown as in eq 16,

$$X_B\gamma_B = X_{B,aq}\gamma_{B,aq} \tag{16}$$

where subscript aq represents the aqueous phase. The same is true for the distribution between another organic phase and the aqueous phase (eq 17). The superscript prime for the

$$X_B'\gamma_B' = X_{B,aq}\gamma_{B,aq} \tag{17}$$

organic phase will be used to distinguish one organic phase from another.

If one assumes that the activity of B in the aqueous phase which is chosen as a reference phase is the same in all systems, then

$$X_B/X_B' = \gamma_B'/\gamma_B \tag{18}$$

Accordingly the ratio of the distribution coefficients of a solute B in two systems with different organic phases can be predicted as the ratio of reciprocals of the activity coefficients of B in the corresponding organic solvent pair.

The so-called distribution coefficients of acetylacetone between an aqueous phase and many organic phases have been published, but these reported values of distribution coefficients are apparent ones determined experimentally and are the mixed values of the distribution coefficients of enol and keto forms of acetylacetone. Actually, acetylacetone is in a tautomerization equilibrium in both phases. The intrinsic distribution coefficient must be defined as the distribution ratio of the *single* chemical species. The distribution coefficient of the enol tautomer alone, K_{DE}, is given by eq 19 (*17*, *19*), and that of the keto tautomer,

$$K_{DE} = D_A\frac{K_e}{K_a}\,\frac{1}{1 + K_{org}} \tag{19}$$

K_{DK}, is given by eq 20, in which D_A is the apparent distribution

$$K_{DK} = D_A\,\frac{1}{(1/K_{org} + 1)(1 - K_a/K_e)} \tag{20}$$

coefficient of acetylacetone, K_a and K_e are the acid dissociation constant of acetylacetone and that of the enol tautomer of acetylacetone in the aqueous solution, and K_{org} is the concentration ratio of the keto and enol forms at infinite dilution in the organic phase. K_a and K_e for acetylacetone are reported as 1.17×10^{-9} (*15*) and 6.88×10^{-9} (*16*), respectively, and K_{org} at infinite dilution is given in Table VII, which is calculated from coefficient C in Table IV. According to eq 19 and 20, K_{DE} and K_{DK} can be obtained separately from the apparent distribution coefficients of acetylacetone determined by Suzuki et al. (*17*) and Rydberg et al. (*14*).

The value of K_{DE} in an organic solvent system relative to K_{DE} in the carbon tetrachloride system, $K^x{}_{DE}/K^x{}_{DE,CCl_4}$ in terms of mole fraction, in which the carbon tetrachloride system is chosen arbitrarily as a reference system, can be compared with the relative value of the thermodynamic activity coefficient of the enol tautomer in the corresponding system ($1/\gamma_E{}^{\infty}$). These results are summarized in Tabel VII. It is noted that, except for the chloroform system, the distribution coefficients of the enol tautomer estimated from the overall distribution coefficients of acetylacetone are close to those predicted from the activity coefficients estimated in this study. For the keto tautomer it seems that a consistency between experimental and theoretical distribution coefficients is not so good as in the case of the enol tautomer, and this is partly due to an uncertainty in the exact determination of the smaller K_{org} value.

No satisfactory explanation for the difference between calculated and experimental values in the chlorofrom system can be given, but we suspect it to be due to greater mutual solubility of water and chloroform in the liquid–liquid partition experiment, where the activity coefficient will surely be modified and a different value of the activity coefficient of each tautomer would be appropriate. The possibility of an association of acetylacetone with water dissolved in the organic phase has been discussed (*18*). This may partly explain the discrepancy in the chloroform system.

In conclusion, the thermodynamic quantities of the enol and keto tautomers of acetylacetone in five organic solvent systems have been estimated, and a comparison of the experimental distribution coefficients of the tautomers with those calculated from the activity coefficients has been demonstrated. These results will be very valuable not only in the field of solution chemistry but also in the field of solvent extraction chemistry (*19*).

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Surface Tension of $NaCl–AlCl_3$ Melts

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Surface tensions have been measured in the range of mole fractions 0.5 < N_{AlCl_3} < 0.6 and temperatures 412 < T <667 K. The results can be expressed by $\gamma/(\mathrm{mN\ m^{-1}}) = 212.7 - 0.0394T - 451N_{AlCl_3} + 306(N_{AlCl_3})^2$ with a root mean square deviation of ±0.74 mN m^{-1}.

There are no measurements of the surface tension of $NaCl–AlCl_3$ melts reported in the literature. Of the methods available, the maximum bubble-pressure method was chosen as requiring a very simple apparatus and not needing an accurate knowledge of the contact angle. Capillary rise measurements were found to be unreproducible, apparently because the contact angle against glass is very variable.

The pressure (p) required to blow a hemispherical bubble on the end of a capillary tube immersed to a depth d below the surface of a liquid is

$$p = 2\gamma/r + g\rho d \qquad (1)$$

where γ is the surface tension, r is the radius of the bubble, and ρ is the density of the liquid. The maximum pressure observed just before the bubble detaches comes when r is equal to the radius of the tube; if the contact angle is less than 90°, as it is in this case, the internal radius is taken, and, if the contact angle is greater than 90°, the external radius of the tube is used. Apart from this, knowledge of the contact angle does not enter into the calculation. By making measurements at two different values of d, one can determine both γ and ρ.

Equation 1 is not quite exact since, in practice, the bubble formed is not exactly hemispherical. Correction tables are given by Adam (*1*), together with a discussion of the method in general.

Experimental Section

The apparatus is shown in Figure 1. A Chromel "A" heater was wound directly on a 25-mm o.d. Pyrex tube, with two strips of asbestos tape down the sides to prevent it from slipping. It was then put inside a 35-mm tube which served as heat insulation. The melt was stirred by bubbling dried argon through it, and its temperature was measured with a platinum—platinum–10% rhodium thermocouple. Temperature control was manual by means of a Variac.

Table I. Surface Tension and Density Measurements

N_{AlCl_3}	T, K	density, kg m^{-3}	surface tension, mN m^{-1}
0.520	486	1635	42.6
(0.520)	446	1694	43.7
(0.519)	526	1608	41.3
(0.518)	568	1592	39.5
(0.515)	616	1550	37.7
0.515	437	1695	44.7
0.511	677	1504	35.9
0.506	477	1663	44.9
0.505	577	1590	40.6
(0.505)	520	1635	43.0
(0.503)	652	1548	37.9
0.500	473	1675	44.9
(0.500)	544	1618	42.3
(0.499)	603	1551	38.1
(0.498)	676	1529	36.9
0.499	474	1679	45.2
(0.498)	647	1551	38.1
(0.600)	412	1720	35.9
0.596	475	1634	33.0
0.534	481	1653	38.9
(0.534)	429	1684	41.2
0.533	537	1614	37.8
(0.529)	615	1557	36.0
(0.527)	528	1620	39.0
(0.526)	458	1678	41.6
0.526	431	1690	42.5
(0.578)	412	1689	38.7
0.575	436	1673	37.2
0.603	419	1673	36.3

Capillary tubes were drawn and selected to have a diameter of ~0.7 mm; the exact diameter was measured on a metallographic microscope. A slow stream of argon (10–20 bubbles/min) was dried with magnesium perchlorate and passed through. It was found essential not to have any rubber tubing after the drying agent or the capillary became blocked with a gelatinous deposit (presumably Al_2O_3). The pressure was measured on a dibutyl phthalate manometer; a 1-L ballast flask connected to the system made the pressure oscillation slower and less extreme. With an interval of 5–10 s between bubbles,

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