Vapor–Liquid Equilibrium of the System Methyl Ethyl Ketone–*sec*-Butyl Alcohol

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Vapor–liquid equilibrium of the system methyl ethyl ketone–*sec*-butyl alcohol has been investigated experimentally. Data obtained from isobaric determinations at three different total pressures have been treated thermodynamically taking into account all deviations from ideality. The procedure leads to an excellent agreement between recalculated and experimental points appearing as a valid tool for a correct prediction of the equilibrium over a wide range of operating conditions.

The purification of methyl ethyl ketone (MEK) from *sec*-butyl alcohol (SBA) by distillation is the final step of the ketone manufacturing process. Two sets of V–L equilibrium data concerning this system, obtained by different authors, are reported in the literature (*1*, *4*). However a substantial disagreement between them and the lack of any attempt at thermodynamic interpretation suggested the need for a new and more extensive experimental work followed by a rigorous thermodynamic treatment of the results so as to characterize the equilibrium over a wide range of pressures and temperatures.

Experimental Section

Heat of mixing and V–L equilibrium compositions and temperatures were measured under three total pressures, namely, 200, 500, and 760 mmHg. Additionally, vapor pressures of individual components were also determined, mainly as a check of quality of the products.

Chemicals. Carlo Erba analytical grade MEK and SBA were used in the work. Both reagents were purified further by repeated distillations until the constancy of normal boiling points and refractive indexes was reached. The final values of these properties are the following; the corresponding accepted literature data (*2*) are indicated in parentheses for comparison.

	Normal bp, °C		Refractive index	
MEK	79.6	(79.59)	1.3762	(1.37643)
SBA	99.5	(99.55)	1.3949	(1.3949)

Apparatuses and Procedures. Integral heat of mixing was determined by measuring the temperature variations accompanying individual additions of one or another pure component to known mixtures. A LKB precision adiabatic calorimeter was employed for this purpose (*8*). The amount of each addition, made by an automatic burette, was such to keep the temperature variation within 4 °C of the nominal value.

For V–L determinations a modified Gillespie-type, two-phase recirculation still was employed. Details of the apparatus are reported elsewhere (*7*); a further innovation introduced this time was moderate magnetic stirring within the boiling chamber in order to avoid local superheating of the liquid. During the runs the pressure was maintained ±0.5 mmHg around the nominal value by means of an electronic regulator connected to the condenser top; the corresponding equilibrium temperatures were read with an accuracy of ±0.05 °C on a digital thermometer whose probe was immersed in the mercury filling the temperature well of the still. The equilibrium compositions were evaluated by reading the refractive indexes of condensed samples withdrawn from the still on a precision Abbe refractometer whose cell was kept at 25 ± 0.05 °C. The conversion to MEK mole fractions was made through a standard plot prepared from known samples, whose shape allowed a uniform accuracy of ±0.001.

Table I. Heat of Mixing Experimental Data at 40 °C

x_1	H^E, cal/mol	x_1	H^E, cal/mol
0.054	90.95	0.496	393.13
0.110	171.04	0.528	392.18
0.114	178.33	0.533	390.70
0.171	239.21	0.625	368.69
0.233	294.86	0.753	296.15
0.243	304.90	0.760	285.57
0.379	374.88	0.822	231.68
0.421	386.24	0.879	172.93
0.459	391.67	0.883	165.92
0.489	390.53	0.942	88.56

Table II. Vapor–Liquid Equilibrium Experimental Data

P, mmHg	t, °C	x_1	y_1	γ_1^{298}	γ_2^{298}
200	62.90	0.080	0.258	1.9711	1.0244
	59.10	0.174	0.430	1.5823	1.0730
	55.90	0.258	0.544	1.4327	1.1424
	55.50	0.268	0.571	1.4607	1.1145
	53.80	0.320	0.632	1.4056	1.1360
	50.70	0.462	0.743	1.2278	1.2151
	48.20	0.582	0.810	1.1398	1.3573
	46.55	0.695	0.866	1.0690	1.4688
	44.90	0.792	0.915	1.0494	1.5382
500	84.95	0.081	0.200	2.1020	1.0064
	81.75	0.183	0.363	1.6452	1.0432
	79.30	0.268	0.463	1.4332	1.1073
	78.70	0.278	0.480	1.4466	1.1175
	76.50	0.372	0.593	1.3484	1.1316
	74.60	0.473	0.678	1.2290	1.1929
	74.30	0.484	0.685	1.2196	1.2116
	72.80	0.582	0.749	1.1260	1.3156
	70.90	0.702	0.830	1.0672	1.4260
	69.30	0.803	0.890	1.0350	1.5749
	67.50	0.953	0.973	0.9970	1.9384
760	96.50	0.088	0.192	2.1273	0.9877
	90.60	0.278	0.468	1.5498	1.0648
	88.10	0.383	0.583	1.3963	1.1096
	87.20	0.467	0.644	1.2430	1.1699
	86.80	0.478	0.655	1.2427	1.1804
	85.20	0.582	0.737	1.1541	1.2480
	83.30	0.702	0.823	1.0897	1.3463
	81.80	0.803	0.885	1.0477	1.4935
	81.30	0.855	0.905	1.0129	1.7766
	80.60	0.900	0.940	1.0151	1.7350

Boiling points of pure components corresponding to several total pressures were determined by a Swietoslawsky-type glass ebulliometer (*3*). The pressure control and temperature reading device were identical with those in use for V–L equilibrium.

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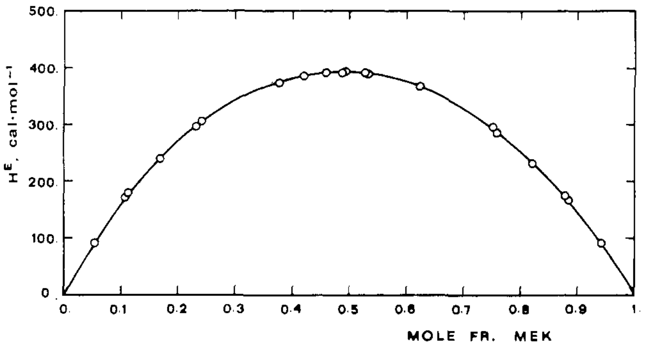

Figure 1. Integral heat of mixing at 40 °C.

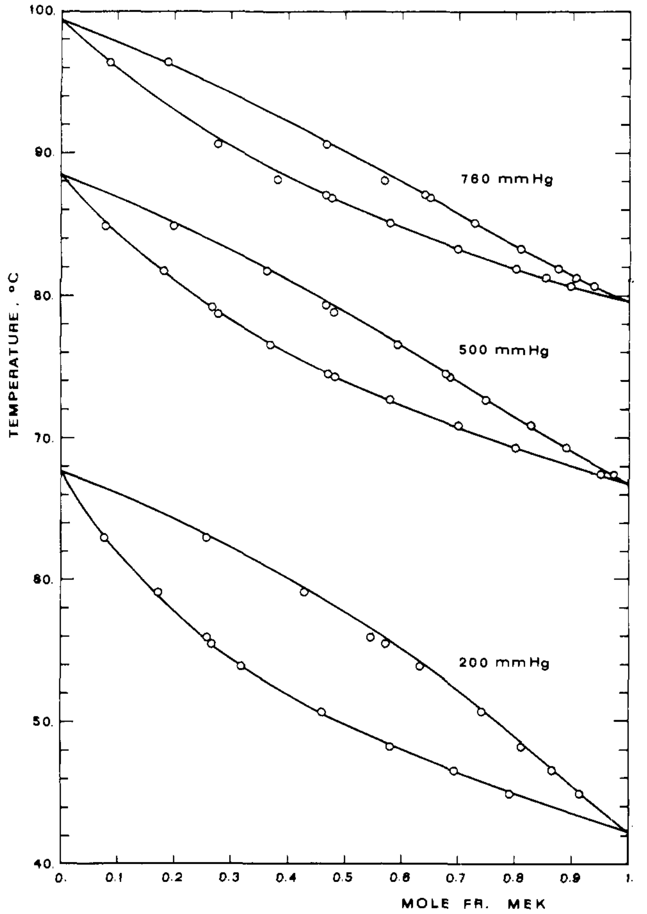

Figure 2. Isobaric vapor-liquid equilibrium diagrams.

Results and Their Correlation

The experimental results of heat of mixing and of V-L equilibrium are shown in Table I and Figure 1 and in Table II and Figure 2, respectively. Vapor pressure data (15 points for each component in the range 10-1000 mmHg) are not reported since they resulted in agreement with reliable literature data (*2*,*5*) within ±3 mmHg. In an attempt to obtain the most accurate interpretation of V-L equilibrium, the most general thermodynamic expression was considered

$$y_i\bar{\nu}_iP = x_i\gamma_i\nu_i{}^\circ P_i{}^\circ \exp\left(\int_{P_i{}^\circ}^{P}(v_{\mathrm{L}i}/RT)\mathrm{d}P\right) \qquad i = 1, 2 \tag{1}$$

from which the activity coefficients can be derived for each experimental point, having measured or evaluated all other terms. The ratio $\bar{\nu}_i/(\nu_i{}^\circ \exp(\int_{P_i{}^\circ}^{P}(v_{\mathrm{L}i}/RT)\mathrm{d}P))$ was calculated following the procedure suggested by Prausnitz (*6*) and successfully applied in several previous works. The properties of pure components necessary for this purpose were all taken from the literature (*2*); they are summarized in Table III. It must be pointed out, however, that in the range of pressures experienced this ratio varied from 0.97 to 1.03, so that no significant error would be introduced by assuming it as equal to 1.

Table III. Pure Component Properties

	$\ln P^\circ = A - B/(T + C)$						
	A	B	C	T_c, K	P_c, mmHg	v_c, cm³/mol	v_L, cm³/mol
MEK	16.310 65	2971.54	−45.60	535.6	31 160	267.06	92.6
SBA	15.659 70	2217.73	−126.86	536.0	31 456	268.56	95.3

Table IV. Parameters of Heat of Mixing Equation

d_1	d_2	d_3
1570.50	−75.20	173.45

Table V. Parameters of Activity Coefficient Equations

	D_1	D_2	D_3
At 298 K	0.782	−0.044	0.052
vs. T	−1.878 + 793.18/T	0.083 − · 37.98/T	−0.242 + 87.60/T

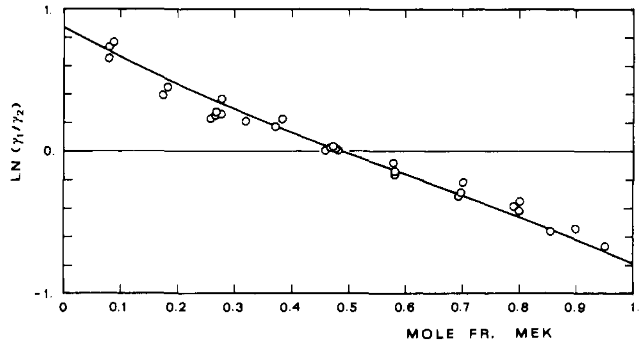

Figure 3. Thermodynamic consistency test.

The activity coefficients determined in this way were then reported to a common reference temperature of 25 °C in order to check their thermodynamic consistency. The heat of mixing measured at 40 °C was used for this correction. Heat of mixing was correlated to the mixture composition by the Redlich-Kister equation

$$H^{\mathrm{E}} = x_1x_2[d_1 + d_2(x_1 - x_2) + d_3(x_1 - x_2)^2] \tag{2}$$

obtaining by regression through the experimental points the values of d_k reported in Table IV.

The isotherm activity coefficients, also indicated in Table II, appear thermodynamically consistent, well satisfying the condition $\int_0^1 \ln (\gamma_1/\gamma_2)\, \mathrm{d}x_1 = 0$, as is shown in Figure 3. They were correlated to the mixture composition once again by the Redlich-Kister equation

$$\ln \gamma_i = (1 - x_i)^2[D_1 - (-1)^iD_2(4x_i - 1) + D_3(2x_i - 1)(6x_i - 1)] \qquad i = 1, 2 \tag{3}$$

obtaining by regression the values of D_k reported in Table V. Remembering that the following conditions hold between d_k and D_k

$$\frac{\partial D_k}{\partial T} = -\frac{d_k}{RT^2} \qquad k = 1, \ldots, 3 \tag{4}$$

D_k can be expressed directly as functions of the temperature as is also reported in Table V.

Based on this characterization of all the deviations from ideality, the liquid and vapor curves were recalculated at the three experimental pressures and superimposed to the points as shown in Figure 2. The agreement appears quite satisfactory, which indicates the suitability of the obtained parameters for the prediction of equilibrium conditions over a fairly extended range of total pressures.

Glossary

A, B, C	parameters of Antoine equation for vapor pressure
d	parameters in eq 2
D	parameters in eq 3
H^E	heat of mixing, cal/mol
P	total pressure, mmHg
P°	vapor pressure, mmHg
R	gas constant, cal/(K mol)
t	temperature, °C
T	absolute temperature, K
v	molar volume, cm^3/mol
x	liquid mole fraction
y	vapor mole fraction

Greek

γ	activity coefficient
ν	fugacity coefficient

Subscripts

c	critical
i	index of component
k	index of parameter in eq 2 and 3
L	liquid phase
1	MEK
2	SBA

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Activity Measurements in Aqueous Mixed Electrolyte Solutions. 1. Hydrochloric Acid–Quaternary Ammonium Chloride Mixtures of Constant Total Ionic Strength

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Emf measurements have been made in cells without liquid junction of the type Pt;H_2(1 atm)|HX(m_1),MX(m_2)|AgCl;Ag, containing mixtures of (i) HCl and $(CH_3)_4NCl$ and (ii) HCl and $(C_2H_5)_4NCl$, in different proportions, but at constant total ionic strength (μ = 3, 2, 1, 0.5, 0.2, 0.1). Measurements have been carried out at 10 °C intervals, over the temperature ranges 5–35 °C. The Ag|AgCl electrodes used, prepared by the thermoelectrolytic method, gave closely agreeing results. The values for the standard electrode potential E° and the interaction coefficient α_{12} for each constant total ionic strength mixture at all the four temperatures have been evaluated by the computerized least-squares method. Interpretation of the results has been made in the light of the recent work of Pitzer.

Introduction

The determination of the activity coefficient of one electrolyte in the presence of another has evoked interest for a fairly long time. The recent spurt in this interest, attributable chiefly to the practical problem of desalination, has stimulated development of the underlying theory and also accumulation of precise experimental results.

The specific ionic interaction principle postulating the existence of short-range interactions among ions of unlike charge was enunciated by Bronsted (*2–4*) and was applied to dilute solutions by Guggenheim (*13–15*). Modifications were suggested for concentrated solutions by Scatchard (*46*, *47*). Pitzer and Brewer (*34*) used the Guggenheim equations with Scatchard modifications (*46*) (BSG theory) to give a simple and compact summary of experimental data. Scatchard et al. (*48*) have subsequently extended and elaborated the Guggenheim equations in several ways leading to very complex formulas for the osmotic and activity coefficients. On this basis Lietzke and Stoughton (*28*) have been able to represent accurately the osmotic coefficients of a number of pure electrolytes; also several systems of mixed electrolytes have been treated. Pitzer (*35*) has recently developed, in a general form, a system of equations for the thermodynamic properties of pure and also mixed electrolytes by using an "electrostatic term" plus a virial coefficient series in which the coefficients may be functions of the ionic strength of the solution. The observed osmotic coefficients of a large number of pure electrolytes of different valence types have been fitted (*36–38*) by using a three-parameter equation; also, a large number of binary electrolyte mixtures have been handled with a two-parameter equation. The work of Reilly, Wood, and Robinson (*41*, *42*) is directed primarily to the process of mixing of pure electrolytes. Finally, Friedman and collaborators (*10*, *11*) have made significant advances in the theory on the basis of rigorous statistical mechanical calculations.

Among the experimental methods for the measurement of the activity and osmotic coefficients in mixed electrolyte solutions, the emf measurement method and the isopiestic vapor pressure measurement have been used most widely. Cells without liquid junction of the type Pt;H_2(g, 1 atm)|HCl(m_1),MCl(m_2)|AgCl;Ag

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