Correlation with Other Data. Figure 1 shows relatively good agreement between the present work and the low-temperature heat-capacity measurements of Goodman and Westrum. The ordinate selected for the graph, $(H_T - H_{273.15})/(T - 273.15)$, makes the plot much more sensitive to errors in heat-content measurements than the usual plot of ΔH against T.

Janz *et al.* (6) have measured the heat content of $BaCl_2$ from 892° to 1339° K. Although the experimental data are not listed in the report, they give linear equations for α, β, and liquid $BaCl_2$ which are 0.45, 0.52, and 0.73 kcal. per mole, respectively, greater than the heat contents determined in this study. Janz' equation for α $BaCl_2$ was used to determine the dashed line shown in Figure 1. Their results for the β and liquid were too high to allow plotting in Figure 1.

Analysis of the data presented here indicates a solid state transition at 1198° K. with a heat effect of 4.05 kcal. per mole. Dworkin and Bredig (*1*) give 1193° K. and 4.10 kcal. per mole for this transition, while Janz *et al.* give 1198° K. and 4.15 kcal. per mole.

The value for the heat of fusion, 3.90 kcal. per mole at 1233° K., as determined by Dworkin and Bredig, is only 2% higher than the value, 3.82 kcal. per mole at 1235° K., determined in this work. The value obtained by Janz *et al.*, 4.13 kcal. per mole at 1235° K., is 8% higher than obtained in this work and would appear to be too high. Popov and Gal'chenko (*9*) report a C_p equation for $BaCl_2$ from 443° to 973° K. Their equation gives values which range from 4% at 450° K. to 8% at 950° K. higher than the results of this investigation.

From the height of the peaks of a DTA curve made on a sample of $BaCl_2$, the ratio ΔH transition/ΔH fusion was calculated to be 1.06. This compares with similar ratios of 1.06 for this investigation, 1.05 for Dworkin's work, and 1.00 for Janz'. The data for the β crystal form (1200° to 1235° K.) appear to show a very small transition (0.05 kcal. per mole) at 1221° K.; however, the measurements were not considered precise enough to establish definitely the existence of this transition.

NOMENCLATURE

α $BaCl_2$ = low-temperature orthorhombic form of barium chloride
β $BaCl_2$ = high-temperature face-centered cubic form of barium chloride
C_p = heat capacity, cal./mole ° K.
1 cal. = 4.1840 absolute joules
H_T = heat content at temperature T
H_0° = heat content at 0° K.
ΔH_T = heat of transition
ΔH_f = heat of fusion
S° = absolute entropy, eu.
T, ° K. = absolute temperature, degrees Kelvin

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Isobaric Vapor-Liquid Equilibrium Data for the Systems 1-Propanol–Methylcyclohexane and Methylcyclohexane–1-Butanol

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Vapor-liquid equilibrium data for the binary systems, 1-propanol–methylcyclohexane and methylcyclohexane–1-butanol, were obtained at 760 mm. of mercury by using a vapor recirculatory equilibrium still. The data are correlated satisfactorily by the Wilson equations.

DISTILLATION operation has been extensively used for the separation of liquid mixtures. Accurate and complete vapor-liquid equilibrium data for the mixtures under consideration are necessary for the rational design of distillation towers. These data are obtainable under two fixed conditions, isothermal and isobaric. Most distillation processes are carried out at constant pressure rather than constant temperature, so that temperature-composition curves are more practical in engineering calculations such as the number of plates, although from theoretical considerations pressure-composition curves are preferable. As part of a continuing equilibrium study of the important alcohol-hydrocarbon systems, hitherto unreported vapor-liquid equilibrium data on 1-propanol–methylcyclohexane and methylcyclohexane–1-butanol systems were determined at 760 mm. of mercury.

EXPERIMENTAL

Purity of Liquids. Analytical reagent grade liquids were used. 1-Butanol (British Drug Houses, India) and 1-propanol (Veb Labor Chemie Apolda, Germany) were further purified by refluxing over fresh quicklime for 6 hours and distilling in a 3 × 100 cm. glass column packed with McMahon packings. Methylcyclohexane (E. Merck, Germany) was distilled in the same column. The predistillate and residual liquids, each approximately one sixth of the original charge, were discarded and the heart cuts were used. Precautions were taken to minimize absorption of atmospheric moisture by the liquids. The physical properties

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of the compounds used are listed with literature data (*8*) in Table I.

Analytical Method. Refractive index measurements were adopted to analyze vapor and liquid samples from the still because of the wide difference between the refractive indices of the pure components in each binary system. An Abbe refractometer controlled at 25° ± 0.2° C. was used. The measurements were reproducible to within ±0.0002. Calibration data are shown in Table II.

Apparatus. Equilibrium data were obtained using a vapor recirculatory equilibrium still designed by Raju, Ranganathan, and Rao (*7*). Mercury-in-glass fractional thermometers were used to measure temperatures to within ±0.1° C. Observed temperatures were corrected to 760 mm. of mercury by Equation 1 (*6*)

$$t_c = t_o + 0.00012\,(t_o + 273.2)(760 - \pi) \tag{1}$$

Since atmospheric pressure recorded during experimental work showed only a small deviation from 760 mm. of mercury, pressure effects on the equilibrium data were negligible and no correction was made.

Table I. Physical Properties of Pure Liquids

Liquids	Normal B.P., ° C. Exptl.	Normal B.P., ° C. Lit.	Ref. Index, n_D^{25} Exptl.	Ref. Index, n_D^{25} Lit.
1-Propanol	97.3	97.2	1.3833	1.3835
Methylcyclohexane	100.8	100.9	1.4208	1.4206
1-Butanol	117.8	117.36	1.3980	1.3992 (n_D^{20})

Table II. Analytical Data for Binary Systems

1-Propanol (1)–Methylcyclohexane (2) x_1	1-Propanol (1)–Methylcyclohexane (2) n_D^{25}	Methylcyclohexane (1)–1-Butanol (2) x_1	Methylcyclohexane (1)–1-Butanol (2) n_D^{25}
1.000	1.3833	1.000	1.4208
0.937	1.3867	0.870	1.4179
0.800	1.3937	0.764	1.4144
0.714	1.3975	0.618	1.4125
0.626	1.4010	0.521	1.4100
0.530	1.4047	0.427	1.4080
0.425	1.4082	0.329	1.4062
0.296	1.4122	0.232	1.4032
0.160	1.4161	0.155	1.4014
0.000	1.4208	0.072	1.3997
		0.000	1.3980

RESULTS AND THERMODYNAMIC ANALYSIS

Experimental results are given in Tables III and IV; the liquid phase activity coefficients were calculated by the expression (*1*):

$$\ln\frac{y_i}{x_i} = \ln\frac{\gamma_i P_i^0}{\pi} - \frac{(V_i - \beta_i)(P_i^0 - \pi)}{RT} \tag{2}$$

The virial coefficients were estimated by the Wohl generalized relation (*1*). The vapor pressure data were obtained by the Antoine equation, taking the numerical values of its constants from Lange (*3*). The molal liquid volumes were determined by the method of Lydersen, Greenkorn, and Hougen (*4*).

Figures 1 and 2 represent boiling point diagrams. Both systems are azeotropic. Azeotropic compositions and temperatures (interpolated values) are:

	x_1	t, ° C.
1-Propanol (1)–methylcyclohexane (2)	0.465	87.0
Methylcyclohexane (1)–1-butanol (2)	0.745	96.5

At constant pressure the exact expression for testing data consistency (*2*) is:

Table III. Vapor-Liquid Equilibrium Data for 1-Propanol(1)–Methylcyclohexane (2) System at 760 Mm. of Hg

Equilibrium Data			Activity Coefficient Data							
Exptl.			Exptl.				Calcd.			
t, ° C.	x_1	y_1	γ_1	γ_2	$\ln \gamma_1$	$\ln \gamma_2$	γ_1	γ_2	$\ln \gamma_1$	$\ln \gamma_2$
93.0	0.050	0.242	5.693	1.003	1.7392	0.0029	5.754	1.010	1.7499	0.0094
88.9	0.100	0.325	4.080	1.035	1.4062	0.0343	4.290	1.033	1.4562	0.0328
88.1	0.200	0.404	2.892	1.086	1.0621	0.0822	2.805	1.1125	1.0312	0.1066
87.4	0.300	0.431	2.108	1.212	0.7455	0.1918	2.084	1.290	0.7344	0.2547
87.1	0.400	0.455	1.687	1.365	0.5232	0.3108	1.674	1.380	0.5150	0.3223
87.0	0.500	0.480	1.430	1.568	0.3578	0.4497	1.431	1.5815	0.3581	0.4584
87.2	0.600	0.492	1.212	1.896	0.1921	0.6401	1.2465	1.843	0.2203	0.6114
87.7	0.700	0.525	1.076	2.360	0.0732	0.8588	1.1325	2.209	0.1243	0.7925
88.3	0.800	0.575	1.017	3.071	0.0168	1.1220	1.065	2.7105	0.0622	0.9971
91.4	0.900	0.720	1.009	3.627	0.0083	1.2884	1.015	3.435	0.0144	1.2341
93.7	0.950	0.832	1.004	4.138	0.0035	1.4203	1.000	4.536	0.0000	1.5120

Table IV. Vapor-Liquid Equilibrium Data for Methylcyclohexane(1)–1-Butanol (2) System at 760 Mm. of Hg

Equilibrium Data			Activity Coefficient Data							
Exptl.			Exptl.				Calcd.			
t, ° C.	x_1	y_1	γ_1	γ_2	$\ln \gamma_1$	$\ln \gamma_2$	γ_1	γ_2	$\ln \gamma_1$	$\ln \gamma_2$
112.5	0.050	0.207	2.833	1.002	1.059	0.0021	3.219	1.003	1.1690	0.0031
108.6	0.100	0.324	2.626	1.046	0.9645	0.0451	2.862	1.012	1.0515	0.0128
104.0	0.200	0.473	2.172	1.098	0.7755	0.0933	2.319	1.051	0.8410	0.0499
101.3	0.300	0.558	1.8415	1.172	0.6106	0.1584	1.933	1.117	0.6588	0.1106
99.4	0.400	0.619	1.616	1.273	0.4800	0.2411	1.650	1.2165	0.5006	0.1958
97.9	0.500	0.665	1.450	1.426	0.3715	0.3550	1.439	1.360	0.3640	0.3078
96.9	0.600	0.706	1.320	1.632	0.2778	0.4896	1.280	1.570	0.2470	0.4510
96.6	0.700	0.733	1.185	2.000	0.1697	0.6932	1.161	1.882	0.1496	0.6324
96.6	0.800	0.756	1.070	2.742	0.0671	1.0087	1.076	2.372	0.0734	0.8637
97.6	0.900	0.824	1.007	3.796	0.0067	1.3339	1.021	3.796	0.0204	1.3340
98.6	0.950	0.895	1.001	4.3125	0.0010	1.4615	1.002	4.794	0.0020	1.5673

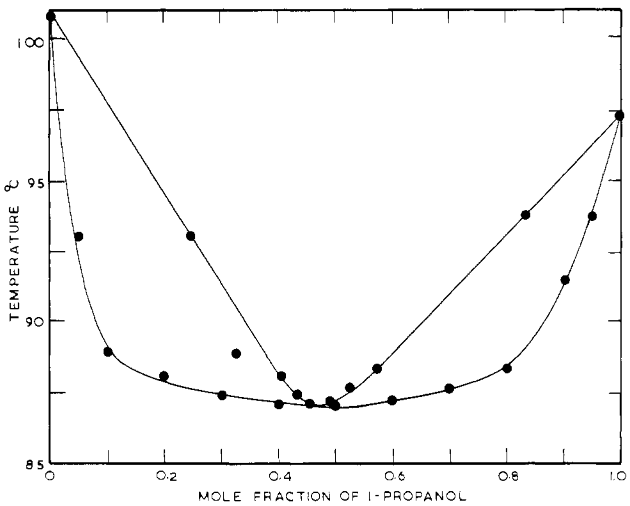

Figure 1. Boiling point diagram for 1-propanol (1)–methylcyclohexane (2) system

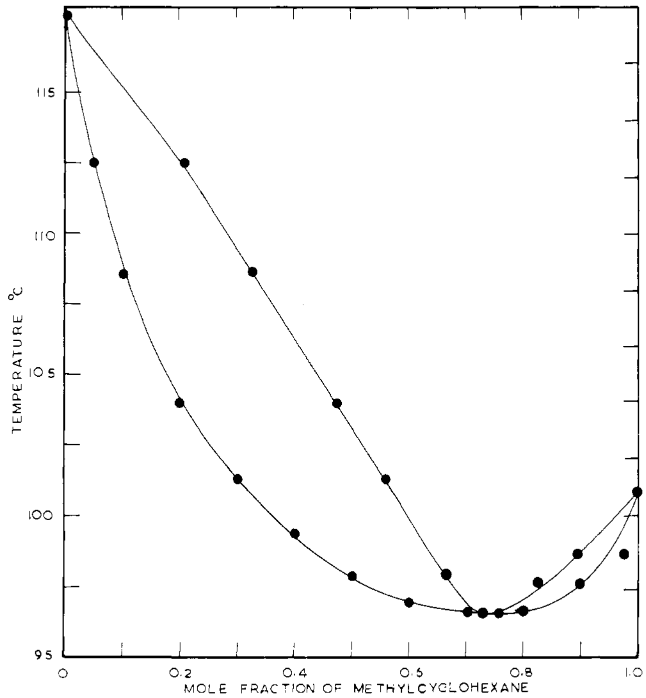

Figure 2. Boiling point diagram for methylcyclohexane (1)–1-butanol (2) system

$$\int_0^{1.0} \ln\frac{\gamma_1}{\gamma_2}\,dx_1 = -\int_0^{1.0} \frac{\Delta H}{RT^2}\left(\frac{dT}{dx_1}\right)_\pi dx_1 = a \tag{3}$$

where ΔH is the heat of mixing of the two components at the temperature, pressure, and composition of the mixture and a is a function of pressure. As the heat of mixing data for the 1-propanol–methylcyclohexane and methylcyclohexane–1-butanol systems were not available, the second term in Equation 3 could not be evaluated. But its value must be small because (dt/dx_1) changes sign over the composition range. The first term of Equation 3 was evaluated between the limits of $x_1 = 0$ and $x_1 = 1.0$ for both systems; the values obtained are 0.0615 and 0.0086 for 1-propanol–methylcyclohexane and methylcyclohexane–1-butanol systems, respectively. These small values suggest that the data are consistent.

The experimental data for both systems were correlated by the modified Wilson equations as suggested by Orye and Prausnitz (5):

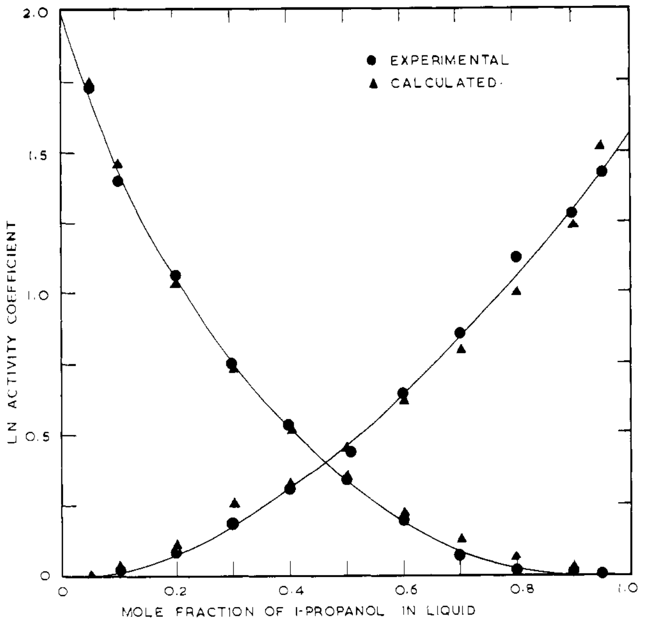

Figure 3. Activity coefficients for 1-propanol (1)–methylcyclohexane (2) system

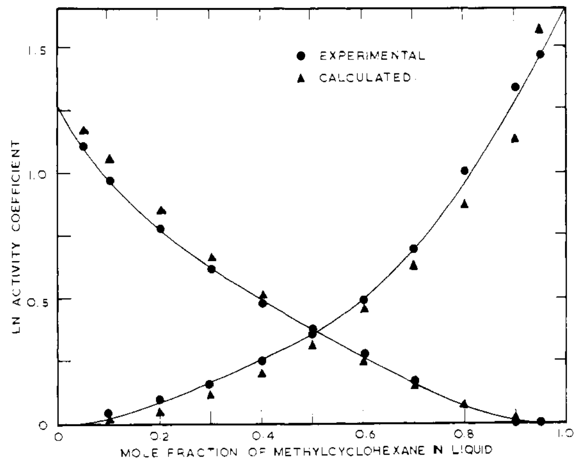

Figure 4. Activity coefficients for methylcyclohexane (1)–1-butanol (2) system

$$\ln\gamma_1 = -\ln(x_1 + \lambda_{12}x_2) + x_2\left[\frac{\lambda_{12}}{x_1 + \lambda_{12}x_2} - \frac{\lambda_{21}}{\lambda_{21}x_1 + x_2}\right] \tag{4}$$

$$\ln\gamma_2 = -\ln(x_2 + \lambda_{21}x_1) - x_1\left[\frac{\lambda_{12}}{x_1 + \lambda_{12}x_1} - \frac{\lambda_{21}}{\lambda_{21}x_1 + x_2}\right] \tag{5}$$

The values of the parameters determined from the experimental data are:

	λ_{12}	λ_{21}
1-Propanol (1)–methylcyclohexane (2)	0.1965	0.4923
Methylcyclohexane (1)—1-butanol (2)	0.5332	0.3326

The activity coefficient–composition data calculated using these binary constants are compared with experimental results in Tables III and IV and Figures 3 and 4. The standard deviations in activity coefficients of both systems were calculated by the expression:

$$\omega_i = \frac{\Sigma K_i^2 - (\Sigma K_i)^2 n_i^{1/2}}{n_i - 1} \tag{6}$$

The values of the calculated deviations are:

	ω_1	ω_2
1-Propanol (1)–methylcyclohexane (2)	−0.00567	0.01987
Methylcyclohexane (1)–1-butanol (2)	−0.21015	0.00475

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NOMENCLATURE

K = algebraic difference between calculated and experimental activity coefficient
n = total number of observations
n_D^{25} = refractive index at 25° C. in sodium light
P^0 = vapor pressure of pure component, mm. Hg
R = gas constant, cal. deg.$^{-1}$ mole^{-1}
t = temperature, ° C.
T = absolute temperature, ° K.
V = molar liquid volume, cc. mole^{-1}
x = mole fraction in liquid phase
y = mole fraction in vapor phase
β = second virial coefficient
γ = liquid-phase activity coefficient
λ = Wilson parameter
π = total pressure, mm. Hg
ω = defined deviation of K from mean value of K, Equation 6

Subscripts

i, 1, 2 = components
12, 21 = binary systems
c = corrected
o = observed

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Vapor-Liquid Equilibrium of Dimethyl Sulfoxide–1-Butanol System

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Vapor-liquid equilibrium data are presented for the system dimethyl sulfoxide–1-butanol at 120.2° and 150.3° C. Equilibrium was attained in a static cell and the analyses were done by refractometry. The Redlich-Kister procedure was used to check the thermodynamic consistency of the data, and the data were correlated with four-constant Redlich-Kister equations.

INDUSTRIAL applications of dimethyl sulfoxide (DMSO) have increased markedly in recent years and this in turn has led to the investigation of many of its properties. This paper presents isothermal equilibrium data for the binary system of DMSO and 1-butanol.

EXPERIMENTAL

Materials. DMSO of 99.9% purity (J. T. Baker Chemical Co., Phillipsburg, N. J.) was further purified by six recrystallizations, giving a yield of 25%. The 1-butanol was of chromatographic quality (British Drug Houses, Poole, England) and was further purified in a fractionating column with 21 sieve plates. The middle fraction corresponding to a temperature of 107.7° C. was collected.

Apparatus and Procedure. The equilibrium cell of borosilicate glass (Figure 1) is a modification of that used by Rabe and Harris (7). All stopcocks were of high-vacuum type, individually ground, and lubricated with Dow Corning silicone high-vacuum grease. Evacuations were carried out to 10^{-6} mm. of Hg, as determined with a McLeod gage on the vacuum line. The constant-temperature bath was controlled to ±0.02° C., and the thermometer was standardized against a quartz thermometer to an accuracy of ±0.01° C.

To load the cell, tube E was first evacuated and stopcock 4 closed. After opening the rest of the cell to the atmosphere, 250 ml. of clean mercury was introduced through side tube D, the mercury attaining level aa′. The cell was evacuated again to remove dissolved gas from the mercury. Bulb B and tube F were filled with this mercury by tilting the cell, and stopcock 5 was turned so that the mercury in bulb B could not fall into bulb A.

A known sample was injected into the side tube C through tube D, frozen with liquid nitrogen, and the cell again evacuated. To remove residual air, stopcock 6 was closed, the sample melted, then refrozen, and again evacuated. This procedure was repeated until residual air was removed.

The cell, disconnected from the vacuum line, was then clamped vertically in the constant-temperature bath, with tube E projecting above the oil level. In this position, with bulb B and F filled with mercury, the mercury reached level bb′. Equilibrium was reached in two and one-half hours of shaking of the cell, after which stopcock 5 was opened so that a vapor sample replaced the mercury in bulb B and an equal volume of mercury entered bulb A from the bottom. Stopcock 5 was closed and 4 opened to tube E. The known volume of vapor collected in bulb A was then frozen in the end of tube E with liquid nitrogen, and removed from the cell by sealing and fusing the glass with a hand torch.

Analytical Technique. The amount of sample collected in the sealed end of tube E was determined by weighing

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