The values of the calculated deviations are:

| | $\omega_1$ | $\omega_2$ |
|---|---|---|
| 1-Propanol (1)–methylcyclohexane (2) | –0.00567 | 0.01987 |
| Methylcyclohexane (1)–1-butanol (2) | –0.21015 | 0.00475 |

## ACKNOWLEDGMENT

The services of S. K. Sawarkar and S. M. K. A. Gurukul are gratefully acknowledged.

## 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
$\beta$ = second virial coefficient
$\gamma$ = liquid-phase activity coefficient
$\lambda$ = Wilson parameter
$\pi$ = total pressure, mm. Hg
$\omega$ = 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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RECEIVED for review February 29, 1968. Accepted January 13, 1969.

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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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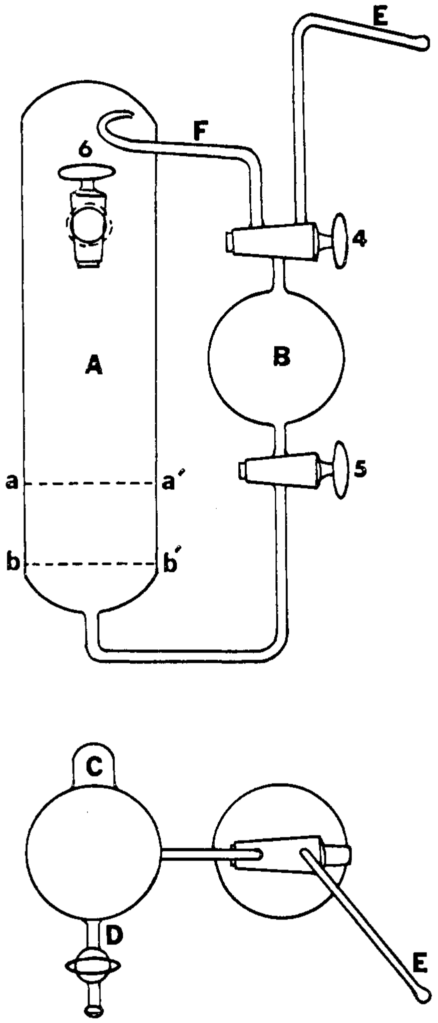

Figure 1. Equilibrium cell

| | |
|---|---|
| *A, B.* | Bulbs |
| *C.* | Side arm into which sample is injected |
| *D.* | Side arm for connection to vacuum line, and introduction of materials |
| *E.* | Vapor collection tube |
| *F.* | Connecting tube |
| *aa', bb'.* | Mercury levels |
| *4, 5, 6.* | Stopcocks |

before and after breaking and emptying. The weight fraction of DMSO in this sample was obtained to an accuracy of ±0.001 by measuring the refractive index, taking the average of two readings, and reading off the weight fraction from a calibration chart. The data in Table I, from which the calibration chart was constructed, give the measured refractive indices of the DMSO-1-butanol system at 25° C., the samples of known composition being prepared by weight. All measurements of refractive indices were made with a Spencer-Abbe refractometer thermostatically controlled at 25° C., using a sodium vapor lamp as the light source.

The mole fraction of DMSO in the liquid phase was calculated by material balance.

## DATA AND ITS CONSISTENCY

The equilibrium data are reported in Table II for temperatures of 120.2° and 150.3° C. For those data in which the pressure was less than 1 atm., the experimental activity coefficients were calculated using the relationship

$$\gamma_1 = \frac{\pi y_1}{P_1^\circ x_1} \tag{1}$$

Table I. Refractive Indices of DMSO–1-Butanol System at 25° C.

| DMSO, Wt. % | Refractive Index |
|---|---|
| 0.00 | 1.39780 |
| 8.91 | 1.40165 |
| 15.04 | 1.40550 |
| 23.33 | 1.41050 |
| 35.64 | 1.41910 |
| 41.33 | 1.42315 |
| 50.50 | 1.42985 |
| 60.07 | 1.43755 |
| 67.58 | 1.44425 |
| 75.29 | 1.45090 |
| 86.78 | 1.46220 |
| 92.77 | 1.46780 |
| 100.00 | 1.47650 |

Table II. Experimental Vapor-Liquid Equilibrium Data for DMSO–1-Butanol System

| Mole % DMSO | | Activity Coefficients | |
|---|---|---|---|
| Liquid $x_1$ | Vapor $y_1$ | DMSO $\gamma_1$ | 1-Butanol $\gamma_2$ |
| | 120.2° C. | | |
| 15.00 | 0.95 | 0.5387 | 0.9979 |
| 26.10 | 2.40 | 0.6658 | 0.9599 |
| 42.02 | 6.55 | 0.8674 | 0.8976 |
| 53.37 | 13.01 | 1.0837 | 0.8041 |
| 65.01 | 21.02 | 1.0703 | 0.7401 |
| 75.68 | 30.57 | 1.0062 | 0.6896 |
| 81.91 | 38.45 | 1.0075 | 0.7084 |
| 89.65 | 49.93 | 1.0103 | 0.7401 |
| 92.80 | 62.68 | 1.0031 | 0.7445 |
| | 150.3° C. | | |
| 12.01 | 1.00 | 0.5084 | 0.9948 |
| 17.68 | 1.41 | 0.5730 | 0.9932 |
| 32.20 | 4.71 | 0.8786 | 0.9720 |
| 40.54 | 8.63 | 1.0924 | 0.9070 |
| 42.93 | 9.40 | 1.0805 | 0.9005 |
| 55.87 | 17.11 | 1.1696 | 0.8231 |
| 64.37 | 24.61 | 1.2017 | 0.7425 |
| 73.46 | 29.98 | 1.1345 | 0.8188 |
| 79.72 | 37.51 | 1.0404 | 0.7389 |
| 84.90 | 45.59 | 1.0467 | 0.7842 |
| 95.49 | 72.03 | 1.0031 | 0.8150 |

The total pressure $\pi$ was calculated from the measured values of volume, temperature, weight, and composition, using the perfect gas law. For the data at high concentrations of 1-butanol (three measurements at 120.2° C. and six measurements at 150.3° C.) where the pressures were estimated to be in the order of 1 atm. or higher, the following relationship

$$\gamma_1 = \frac{\phi_1 y_1 \pi}{x_1 \phi_1^\circ P_1^\circ} \tag{2}$$

was used. The equation of state used for the vapor phase was the virial equation terminated after the second virial coefficient. This leads to the following expressions for the product $\phi_1\pi$ and $\phi_1^\circ$ for substitution into Equation 2.

$$\ln \phi_1 \pi = 2/v\,(y_2 B_{12} + y_1 B_{11}) - \ln\left(\frac{v}{RTy_1}\right) \tag{3}$$

and

$$\phi_1^\circ = 2/v\,B_{11} - \ln\left(\frac{P_1^\circ v}{RT}\right) \tag{4}$$

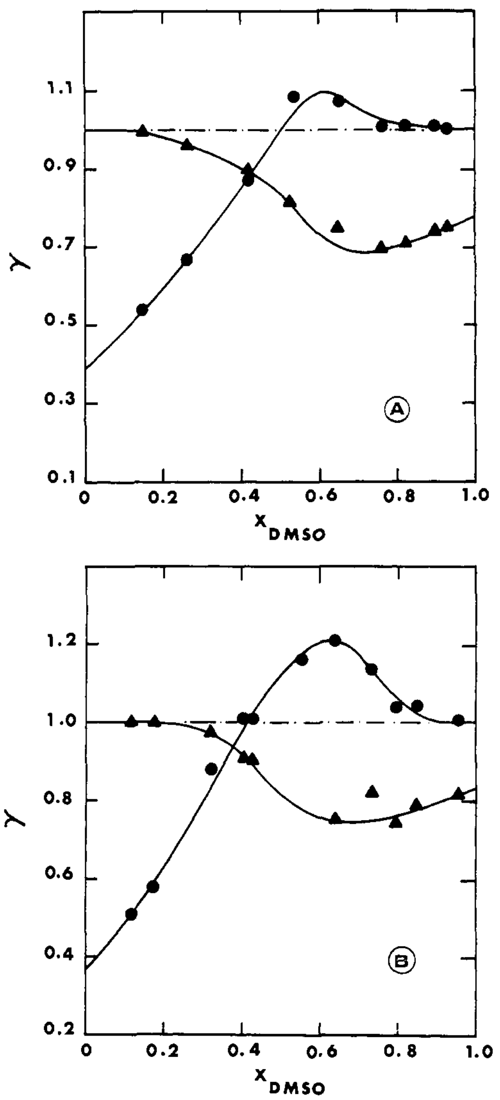

Figure 2. Activity coefficients for DMSO–1-butanol system at (A) 120.2° and (B) 150.3° C.

● DMSO ▲ 1-Butanol

The vapor pressures of the pure components were obtained from the literature (*1*, *3*). The pure-component second virial coefficients and the second virial cross coefficients were estimated by the method of O'Connell and Prausnitz (*4*). The critical constants were obtained from the literature (*6*) for 1-butanol and estimated as $T_c$ = 707° K. and $P_c$ = 61.3 atm. for DMSO by the technique of Fishtine (*2*).

Figures 2*A* and 2*B* are plots of activity coefficients *vs.* mole fraction of DMSO at temperatures 120.2° and 150.3° C., respectively.

The Redlich-Kister procedure (*8*) was used to check the consistency of the data. Plots of log $\gamma_1/\gamma_2$ *vs.* mole fraction of DMSO in the liquid phase are shown in Figures 3*A* and 3*B*. The plots show a difference of less than 2% in positive and negative areas at 120.2° C. and 2.5% for the data at 150.3° C.

The data were correlated with the four-constant Redlich-Kister equation (*9*).

$$\log \frac{\gamma_1}{\gamma_2} = (1 - 2x_1) + C\,[6x_1\,(1 - x_1) - 1] + D(1 - 2x_1)\cdot$$
$$[1 - 8x_1\,(1 - x_1)] + E\,(1 - 2x_1)^2\,[10x_1\,(1 - x_1) - 1] \qquad (5)$$

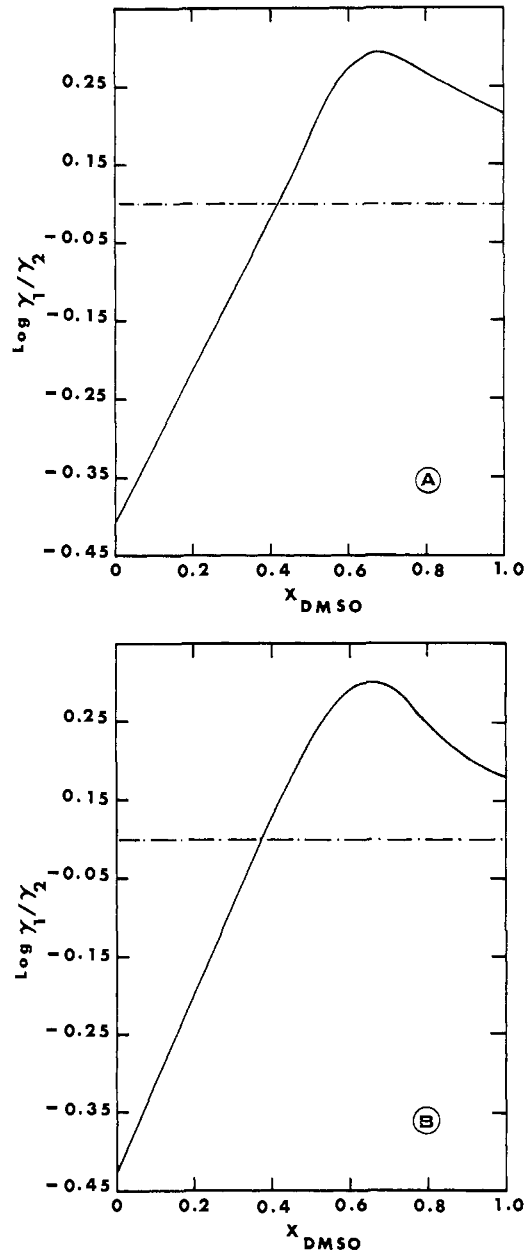

Figure 3. Redlich-Kister plot for DMSO–1-butanol system at (A) 120.2° and (B) 150.3° C.

Table III. Constants of Redlich-Kister Equations for DMSO–1-Butanol System

| 120.2° C. | 150.3° C. |
|---|---|
| $B$ = −0.32280 | $B$ = −0.28821 |
| $C$ = 0.18262 | $C$ = 0.25593 |
| $D$ = 0.06235 | $D$ = 0.04227 |
| $E$ = −0.04185 | $E$ = −0.07915 |

Table III presents the values of the constants at both temperatures.

A statistical analysis (*5*) on the polynomial fit (Equation 5) showed that the fourth degree term is significant and has to be included for 99% confidence level of the *F*-test. The variance of the fit, $\sigma^2$, was 0.00027 at both 150.3° and 120.2° C. The data correlates with the three-constant equation ($E$ = 0) at 95% confidence, and $\sigma^2$ is 0.00075 at 150.3° C., and 0.00038 at 120.2° C. For the two-constant equation ($E$ = $D$ = 0), the data correlates at less than 95% confidence, and $\sigma^2$ is 0.00098 at 150.3° C., and 0.0010 at 120.2° C.

## NOMENCLATURE

$B, C, D, E$ = constants of Redlich-Kister equation
$P^\circ$ = vapor pressure of pure component
$x$ = mole fraction of component in liquid phase
$y$ = mole fraction of component in vapor phase
$\gamma$ = activity coefficient
$\pi$ = total pressure
$\phi$ = fugacity coefficient
$\phi^\circ$ = fugacity coefficient of pure component
$v$ = molar volume
$B_{ij}$ = virial coefficients
$\sigma^2$ = variance of fit

### Subscripts

1 = DMSO component
2 = *n*-Butanol component

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Received for review July 3, 1967. Resubmitted December 20, 1968. Accepted March 10, 1969. Work supported by the National Research Council of Canada.

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# Viscosity Correlation for Mixtures of Freon-12 and Freon-22 Vapors

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**Residual viscosity is a unique function of density for pure Freon-12 and Freon-22 vapors. Also, a plot of residual viscosity against density for Freon-12 and Freon-22 vapors exhibits a regular trend. These phenomena form the basis for predicting the viscosity of mixtures of Freon-12 and Freon-22 vapors.**

THE RESIDUAL viscosity, defined as the difference between the viscosity, $\mu$, at a particular temperature and density, and the viscosity, $\mu_0$, at the same temperature but at zero density (*10*), is a unique function of density for some substances. This concept signifies that a single smooth curve represents the viscosity over a wide temperature and pressure range. The residual viscosity correlation, therefore, serves to represent the experimental viscosity measurements and to predict the viscosity at the temperature and pressure conditions of practical interest.

The correlation technique of residual thermal conductivity of gases and liquids with density, proposed by Abas-Zade, was extended on parallel lines to residual viscosity-density correlation by Shimotake and Thodos (*15*) for liquid and gaseous argon, helium, neon, krypton, and xenon, and by Brebach and Thodos (*1*) for nitrogen, hydrogen, and oxygen in the liquid and gaseous state. The residual viscosity phenomena was confirmed by Dolan *et al.* (*5*) for *n*-butane; by Starling *et al.* (*16*) for propane, and by Eakin *et al.* (*6*) for ethane. The concept was extended successfully to the methane-*n*-butane and methane-propane systems by Dolan *et al.* (*4*). It was also a useful extrapolation technique.

## EMPIRICAL CORRELATIONS

There are four general methods for computing the viscosity of gas mixtures. The method of Hirschfelder *et al.* (*9*), based on rigorous kinetic theory and described by Hirschfelder *et al.* (*8*), is the most reliable, but complicated and time-consuming. Buddenberg and Wilke (*2*) proposed a method based on the Sutherland equation (*17*), eliminating the determinant, but retaining the need for unlike molecular diffusion coefficients. Later, Wilke (*19*) proposed a further development, eliminating even the need for the various unlike molecular diffusion coefficients, and presented a simple equation for gas mixtures. Another method, developed by Herning and Zipperer and successfully employed by Dolan and co-authors (*4*), is significant for its simplicity. This mixing rule is accurate for those mixtures which contain less than 25% hydrogen. Still another method was developed by Dean and Stiel (*3*) for calculation of the viscosity of nonpolar gas mixtures from the molecular weights and critical constants of the components. It claims novelty over the above three methods in enabling computation of viscosity of gas mixtures at moderate and high pressures without viscosity information on the pure components.

## THEORY

For many gases, the residual viscosity can be expressed in terms of density as

$$\mu - \mu_0 = A\rho + B\rho^2 \tag{1}$$

where

$$\mu = \mu(\rho, T)$$

and

$$\mu_0 = \mu(0, T)$$

The coefficients, $A$ and $B$, which depend on the nature of the gas, are only mildly varying functions of temperature (*11*). Equation 1 signifies that if a regular trend exists in the plot of residual viscosity against density for the pure components, then the concept of residual viscosity can be extended to mixtures by relating $A$ and $B$ to composition by the following equations