Isothermal Vapor–Liquid Equilibria for the Systems Toluene–*n*-Heptane, Toluene–Propan-2-ol, Toluene–Sulfolane, and Propan-2-ol–Sulfolane

Stanley J. Ashcroft,* Andrew D. Clayton, and Ronald B. Shearn

Department of Chemical Engineering, University of Exeter, Exeter, Devon EX4 4QF, England

Isothermal vapor pressure data have been measured for the binary systems toluene–*n*-heptane, toluene–propan-2-ol, toluene–sulfolane, and propan-2-ol–sulfolane. Data for the first two systems were obtained at temperatures of 298.15, 303.15, and 313.15 K. For the second two "sulfolane" systems, temperatures of 303.15 and 313.15 K only were used because of the relatively high, 300.95 K, melting temperature of sulfolane. These data were fitted to the NRTL and modified Wilson equations.

Sulfolane has found extensive use in petroleum refining for the recovery, by liquid extraction, of high purity aromatics, particularly benzene, toluene, and xylenes from catalytic reformates. As part of a program to investigate and to predict the phase equilibria present in these multicomponent systems, it became necessary to obtain vapor–liquid equilibrium data for a number of binary systems.

This paper reports the results of these measurements and their correlation by the NRTL and modified Wilson equations.

Experimental Section

Mixture Vapor Pressure Measurements. The vapor pressures of the systems were measured at constant temperature as a function of composition by using a static equilibrium cell. This technique was chosen because of the difficulties encountered in achieving steady boiling in a dynamic equilibrium still when operating at very low pressures. The apparatus, which is described in detail by Clayton (*4*), is shown schematically in Figure 1. It was in some respects similar to those used by several other authors [for example Renon (*14*), Hermsen (*6*), Orye (*9*), and Sassa et al. (*16*)]. Briefly the major items were a large diameter mercury manometer, A, measuring the difference in pressure between the reference high vacuum and measuring manifold systems, and a thermostatic water bath, B, containing the vapor pressure cell assembly, C. The latter consisted of a mercury null manometer, D, connected to the static cell, E. A bypass line, F, connecting the cell with the reference side of the null manometer, was provided to facilitate evacuation of the cell. A Sovirel Torion PTFE barreled stopcock enabled the bypass to be isolated from the cell, while avoiding the contamination problems associated with a greased stopcock. Also located on this bypass line was a ground glass socket, G, so as to afford a connection with the component degassing equipment described by Clayton (*4*). Stirring of the contents of the cell was achieved with a small PTFE-coated magnet, H, activated by a magnetic stirrer motor sited under the water bath.

The mercury levels in both the main and null manometers were read by using Precision Tool and Instrument Co. cathetometers calibrated at 293.15 K. The temperature of the water bath was measured on the IPTS-68 scale with mercury in glass thermometers calibrated against a precision thermometer certificated by the National Physical Laboratory.

Before each experimental run the cell and null manometer were evacuated to below 1.0×10^{-3} mmHg and the cell walls and mercury in the null manometer heated with a torch to desorb any gas present. The components of the mixture were degassed separately in two degassing cells (*4*) by refluxing under vacuum for several hours with a periodic removal of some of the vapor phase. Degassing was assumed complete when successive readings of the pure component vapor pressures differed by less than the error involved in reading the cathetometers. The degassed materials were then transferred under vacuum to the vapor pressure cell via the socket on the bypass line.

In order to make a measurement of the vapor pressure of the cell's contents, the levels in the null manometer were kept as near as possible equal by bleeding dry nitrogen into the measuring manifold while the mixture temperature attained that of the water bath. When there was no further change in the manometer levels these were read with the cathetometers. All manometer readings were corrected for gravity and temperature. The liquid composition was determined by the analysis of samples obtained with a hypodermic needle and syringe inserted into the cell at the end of each run. Refractive index measurements were used for the analysis of the toluene–*n*-heptane, toluene–propan-2-ol, and propan-2-ol–sulfolane mixtures, and gas–liquid chromatography for toluene–sulfolane. The analyses were considered to be accurate to ±0.0005 in mole fraction for the refractive index measurements, and to ±0.001 for the GLC data.

The water bath temperature was controlled to better than ±0.02 K and the calibrated thermometers used made it possible to measure the temperature of the water bath to ±0.02 K. This corresponds to an error of ±0.011 kN m^{-2} or 0.09% in the vapor pressure of *n*-heptane at 313.15 K. Further, it was concluded that the manometric measurements were accurate to ±0.02 mm. The combined effect of the maximum manometric and temperature errors would yield a maximum error in the vapor pressure of *n*-heptane at 313.15 K of ±0.022 kN m^{-2} or 0.18%.

Analytical Instruments. Refractive index measurements were made by means of a Bellingham and Stanley Abbe refractometer, Type 60ED, operating with prisms controlled at a temperature of 303.15 ± 0.02 K. Readings were taken for the mercury e line, wavelength 5.461×10^{-7} m.

A Pye-Unicam Series 104 gas–liquid chromatograph, equipped with a thermal conductivity detector, was used in conjunction with a Honeywell linear amplifier and integrator. The columns were 0.9 m × 3 mm i.d. stainless steel charged with 10 mass % Apiezon L on Chromosorb W, and the carrier gas was helium. The chromatograph was calibrated by the method of Smith and Bowden (*18*).

Sulfolane Vapor Pressure Measurements. These measurements were carried out with a Smith and Menzies isoteniscope connected to the reference manifold of the static cell apparatus. In this case the manometer of the isoteniscope was filled with degassed sulfolane. The reference manifold was held at an indicated pressure of less than 1.0×10^{-3} mmHg with the oil diffusion pump. The vapor pressures were read on one of the cathetometers used with the static cell apparatus. The density data used for pure sulfolane were those of Casteel and Sears (*3*).

0021-9568/79/1724-0195$01.00/0

Table I. Physical Properties of the Pure Components

	density at 303.15 K $\times 10^{-3}$/kg m^{-3}		refractive index at 303.15 K^a		melting temp/K	
	this work	lit.	this work	lit.	this work	lit.
n-heptane	0.6747	0.6753 (*20*)	1.384 21	1.38420 (*20*)		
toluene	0.8583	0.8577 (*20*)	1.495 14	1.49514 (*20*)		
propan-2-ol	0.7769	0.7769 (*5*)	1.374 87			
sulfolane	1.2620	1.2619 (*3*)	1.481 14	1.4810 (*17*)	300.95	300.95 (*17*)

^{a} Wavelength 5.461×10^{-7} m except for sulfolane for which the wavelength was 5.895×10^{-7} m.

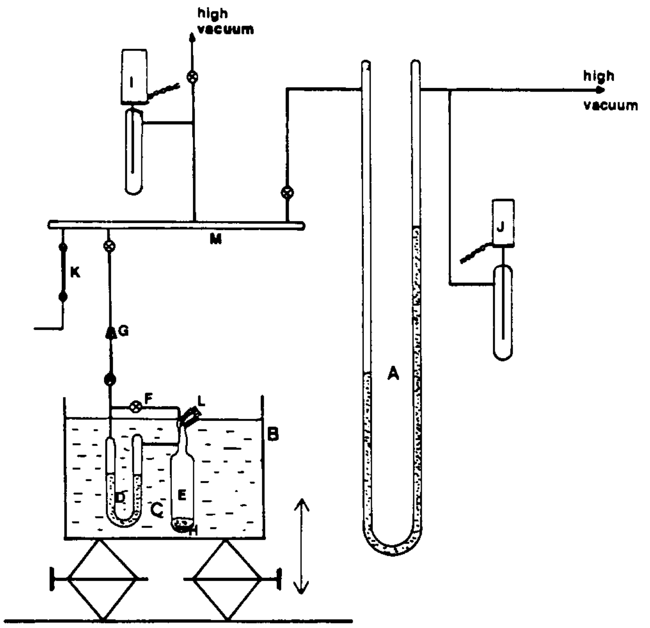

Figure 1. Vapor-liquid equilibrium apparatus: (A) mercury manometer, (B) temperature-controlled water bath, (C) vapor-pressure cell assembly, (D) null manometer, (E) static cell, (F) bypass line, (G) cone and socket, (H) PTFE-coated magnet, (I) Pirani gauge, (J) Penning gauge, (K) dry N_2 bleed line, (L) Torion valve, (M) measuring manifold.

Materials. The toluene and propan-2-ol used were BDH Aristar reagents. These were dried with activated type 5A molecular sieves but otherwise used as supplied. The toluene was certified by the manufacturers to be of a minimum purity of 99.95% w/w and the propan-2-ol to have a maximum water content of 1000 ppm w/w with all other impurities certified to be below 10 ppm w/w. This water content was reduced to below 100 ppm w/w as confirmed by GLC analysis.

The *n*-heptane used was Fison Laboratory reagent. This was passed through a silica gel column (to remove aromatics) and then distilled at atmospheric pressure (25 plate, 25 mm i.d. Oldershaw column, 5:1 reflux ratio). A heart-cut boiling over 0.1 K was taken and stored over molecular sieves.

Anhydrous sulfolane supplied by the Shell Chemical Co. was dried with molecular sieves and then twice vacuum distilled from phosphorus pentoxide at a pressure below 1 mmHg to yield a colorless, odorless product. To minimize the contact of this deliquescent reagent with moist air, the product was kept in stoppered bottles in a desiccator.

Some physical properties of the reagents used are listed in Table I together with literature values.

Results

Table II. Vapor Pressure of Sulfolane

temp/K	vapor pressure/ N m^{-2}	temp/K	vapor pressure/ N m^{-2}
303.15	9.1	318.15	11.9
308.15	9.9	323.15	15.6
313.15	10.5	328.15	21.3

The measured vapor pressures of pure sulfolane between 303.15 and 328.15 K are listed in Table II and those of the binary mixtures in Table III, along with the liquid mole fractions. The binary mixture vapor pressure data were fitted to the NRTL equation of Renon and Prausnitz (*14*, *15*) and also to the modified Wilson equation of Tsuboka and Katayama (*21*), the latter being preferred to the original Wilson equation when required to represent liquid-liquid equilibria. In both cases a linear function similar to that given by Asselineau and Renon (*2*) was used to express the temperature dependence of the equation constants. The technique used for the data fitting was basically that described by Prausnitz et al. (*12*) in which vapor-phase nonidealities were determined from the virial equation, truncated after the second term. In this case, however, Powell's (*11*) nonlinear regression routine was used to determine the equation constants by minimizing the function

$$S = \sum_{i}^{N} \left(\frac{P_{\text{exptl}} - P_{\text{calcd}}}{P_{\text{exptl}}} \right)^2 \times 100$$

where P_{exptl} and P_{calcd} are respectively the experimental and calculated values of the total vapor pressure for mixture i and N is the total number of experimental points.

All the regression analyses were carried out by using double precision arithmetic upon an ICL 4-72 computer.

The calculated excess Gibbs functions of mixing and vapor-phase mole fractions are given in Table III for each mixture. Only the data found with the NRTL equation are shown for simplicity, those found with the modified Wilson equation being essentially the same. The equation constants determined from the regression analyses are given in Table IV. The critical properties and other parameters required for estimating the second virial coefficients with the correlation of O'Connell and Prausnitz (*8*) are listed in Table V. Pure-component molar volumes and vapor pressures for toluene, *n*-heptane, and propan-2-ol were taken from the publications of the Engineering Sciences Data Unit (*5*) and ref 20 and for sulfolane from Table II and ref 3 and 17.

Discussion

Each of the four systems studied demonstrates nonidealities of mixing, but one, toluene-*n*-heptane, only slightly so (max $G^E \approx 330$ J mol^{-1}). The larger deviations from ideality in the other three systems can be expected in view of the highly polar nature of two of the compounds involved, propan-2-ol and sulfolane. One system, namely, toluene-propan-2-ol, exhibits azeotropic behavior, the azeotropic composition being $x_1 \approx 0.36$ at a total pressure of 9.727 kN m^{-2} ($T = 303.15$ K). Further, a study of the $P-x$ curves for toluene-*n*-heptane would suggest that, at temperatures, and therefore, pressures, lower than those used here, this system also displays azeotropic behavior.

Comparison of the isothermal results reported here with literature data appears to be limited to the toluene-*n*-heptane

Table III. Isothermal Vapor-Liquid Equilibrium Data

x_1	P/kN m^{-2}	y_1	G^E/J mol^{-1}
Toluene (1)–*n*-Heptane (2) at 298.15 K			
0.0	6.08	0.0	0.0
0.066	6.13	0.059	66.1
0.161	5.94	0.138	150.2
0.261	5.85	0.216	223.0
0.377	5.73	0.303	284.5
0.564	5.39	0.442	321.8
0.623	5.27	0.490	315.1
0.751	4.90	0.605	265.3
0.860	4.47	0.734	179.3
0.971	4.05	0.929	44.1
1.0	3.75	1.0	0.0
Toluene (1)–*n*-Heptane (2) at 303.15 K			
0.0	7.73	0.0	0.0
0.066	7.65	0.059	67.3
0.161	7.60	0.138	152.9
0.261	7.45	0.216	227.2
0.377	7.28	0.304	289.8
0.564	6.84	0.445	327.9
0.623	6.68	0.493	321.2
0.751	6.32	0.609	270.4
0.860	5.76	0.738	182.8
0.971	5.18	0.931	45.0
1.0	4.94	1.0	0.0
Toluene (1)–*n*-Heptane (2) at 313.15 K			
0.0	12.23	0.0	0.0
0.066	12.21	0.059	69.8
0.161	12.02	0.138	158.6
0.261	11.82	0.217	235.6
0.377	11.53	0.306	300.6
0.564	10.89	0.449	340.2
0.623	10.65	0.498	333.3
0.773	9.83	0.640	280.7
0.860	9.15	0.746	189.8
0.971	8.24	0.934	46.7
1.0	7.89	1.0	0.0
Toluene (1)–Sulfolane (2) at 303.15 K			
0.0	0.00906	0.0	0.0
0.049	0.900	0.992	160.4
0.094	1.576	0.996	294.5
0.104	1.660	0.996	322.5
0.125	1.910	0.997	379.5
0.213	2.733	0.998	588.4
0.292	3.154	0.998	735.2
0.387	3.620	0.999	860.2
0.493	3.889	0.999	930.8
0.568	4.094	0.999	934.3
0.675	4.186	0.999	866.8
0.736	4.273	0.999	786.5
0.846	4.485	0.999	554.4
0.913	4.649	0.999	349.9
0.956	4.780	1.0	189.9
0.974	4.726	1.0	115.5
1.0	4.937	1.0	0.0
Toluene (1)–Sulfolane (2) at 313.15 K			
0.0	0.0105	0.0	0.0
0.049	1.441	0.992	160.0
0.094	2.465	0.996	293.7
0.104	2.650	0.996	321.7
0.125	3.038	0.997	378.5
0.213	4.385	0.998	586.8
0.292	5.063	0.998	733.0
0.387	5.800	0.999	856.9
0.493	6.225	0.999	925.7
0.568	6.593	0.999	927.8
0.675	6.714	0.999	858.3
0.736	6.883	0.999	777.2
0.846	7.243	0.999	545.3
0.913	7.413	0.999	343.1
0.956	7.676	1.0	185.7
0.974	7.705	1.0	112.7
1.0	7.894	1.0	0.0

x_1	P/kN m^{-2}	y_1	G^E/J mol^{-1}
Toluene (1)–Propan-2-ol (2) at 298.15 K			
0.0	5.846	0.0	0.0
0.009	5.954	0.034	46.6
0.080	6.610	0.191	377.7
0.121	6.862	0.239	542.1
0.292	7.297	0.346	1046.9
0.361	7.402	0.375	1177.8
0.375	7.351	0.381	1199.7
0.529	7.282	0.438	1336.7
0.533	7.302	0.440	1337.7
0.666	7.170	0.485	1289.3
0.818	6.963	0.529	991.4
0.882	6.483	0.548	751.9
0.949	5.906	0.605	388.6
0.980	5.315	0.721	166.7
1.0	3.754	1.0	0.0
Toluene (1)–Propan-2-ol (2) at 303.15 K			
0.0	7.794	0.0	0.0
0.009	8.032	0.031	47.8
0.080	8.812	0.179	388.8
0.121	9.162	0.225	558.7
0.292	9.495	0.331	1084.4
0.361	9.727	0.361	1221.8
0.375	9.680	0.366	1244.8
0.529	9.588	0.425	1389.3
0.533	9.579	0.426	1390.4
0.666	9.403	0.473	1339.5
0.818	8.840	0.521	1026.5
0.882	8.568	0.543	776.2
0.949	7.600	0.608	399.3
0.980	6.959	0.728	170.8
1.0	4.937	1.0	0.0
Toluene (1)–Propan-2-ol (2) at 313.15 K			
0.0	13.779	0.0	0.0
0.009	14.169	0.027	50.4
0.080	15.234	0.158	412.3
0.121	15.687	0.201	594.2
0.292	16.297	0.305	1163.6
0.361	16.341	0.334	1314.3
0.375	16.318	0.340	1339.6
0.529	16.054	0.400	1499.2
0.533	16.062	0.401	1500.4
0.666	15.737	0.451	1443.8
0.818	14.610	0.505	1098.4
0.882	13.781	0.535	825.7
0.949	12.108	0.613	420.8
0.980	10.764	0.741	178.9
1.0	7.894	1.0	0.0
Propan-2-ol (1)–Sulfolane (2) at 303.15 K			
0.0	0.00906	0.0	0.0
0.049	1.687	0.996	270.3
0.153	4.137	0.999	757.6
0.226	5.255	0.999	1032.4
0.304	6.205	0.999	1266.1
0.365	6.436	0.999	1405.8
0.549	7.068	0.999	1590.2
0.672	7.129	0.999	1494.0
0.779	7.212	0.999	1237.9
0.901	7.396	0.999	697.8
0.983	7.561	1.0	140.1
0.992	7.685	1.0	67.1
1.0	7.821	1.0	0.0
Propan-2-ol (1)–Sulfolane (2) at 313.15 K			
0.0	0.0105	0.0	0.0
0.049	2.636	0.996	287.3
0.153	6.607	0.999	803.4
0.226	8.304	0.999	1092.9
0.304	10.251	0.999	1337.9
0.365	10.986	0.999	1483.7
0.549	11.957	0.999	1671.6
0.672	12.325	0.999	1566.2
0.779	12.542	0.999	1294.6
0.901	13.003	0.999	727.5
0.983	13.550	1.0	145.7
0.992	13.683	1.0	69.7
1.0	13.780	1.0	0.0

Table IV. Constants of the NRTL and Modified Wilson Equations for Four Binary Systems (Gained from Vapor-Liquid Equilibrium Data)

system	temp range/K	C_1/J mol^{-1}	C_2/J mol^{-1}	C_3	D_1/J mol^{-1} K^{-1}	D_2/J mol^{-1} K^{-1}	D_3/K^{-1}	stand dev[a]	eq[b]
toluene (1)	298.15	−690.2	2188.3	0.3	2.903	−9.478	0.0	0.660	NRTL
n-heptane (2)	313.15	428.5	923.1		3.751	−10.534		0.661	M. Wil
toluene (1)	298.15	3247.3	6386.2	0.539	−4.383	−27.357	2.97×10^{-3}	1.723	NRTL
propan-2-ol (2)	313.15	720.5	7662.0		−88.362	−35.759		2.022	M. Wil
toluene (1)	303.15	1753.3	3770.4	0.494	3.079	11.373	2.54×10^{-4}	0.957	NRTL
sulfolane (2)	313.15	1141.6	4723.2		2.627	2.509		0.910	M. Wil
propan-2-ol (1)	303.15	2249.4	5893.2	0.341	−25.803	−19.691	3.31×10^{-4}	1.426	NRTL
sulfolane (2)	313.15	3030.8	8944.7		−25.986	−81.684		2.417	M. Wil

[a] The standard deviation of the fit = $\{\Sigma_i^N[P_{\text{exptl}} - P_{\text{calcd}})/P_{\text{exptl}} \times 100]^2/(N - \text{m})\}^{1/2}$. Where *m* is the number of equation constants fitted. [b] The NRTL and modified Wilson equations are given in the Appendix.

Table V. Critical Properties (*5*) and Parameters Characterizing Vapor-Phase Nonideality

component	T_c/K	P_c/MN m^{-2}	V_c/cm^3 mol^{-1}	ω[b]	ω_H[b,c]	μ/D	η
n-heptane	540.1	2.736	431.6	0.3507			
toluene	591.8	4.104	316.2	0.2644			
propan-2-ol	508.3	4.762	220.0	0.6693	0.187	1.66	0.65
sulfolane	776.0[a]	5.066[a]	282.9[a]	0.8608	0.2727	4.69	

[a] Calculated by Lydersen's method as recommended by Reid and Sherwood (*13*). [b] Calculated from $\omega = \log (P_i^0/P_c) - 1.0$, where P_i^0 is taken at $T/T_c = 0.7$. [c] The homomorph of propan-2-ol was taken as 2-methylpropane, ω_H from ref 12, and the homomorph of sulfolane as 1,1-dimethylcyclopentane, ω_H from ref 10.

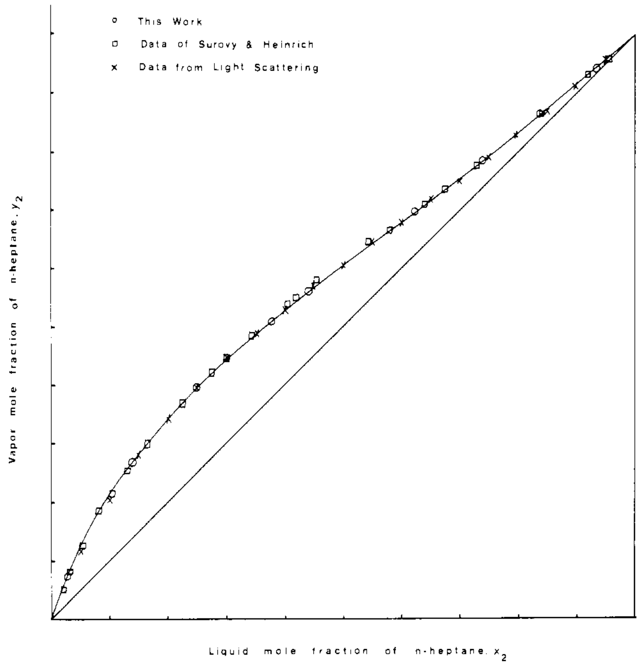

Figure 2. Vapor–liquid equilibrium for the system toluene (1)–*n*-heptane (2). Data are from the present work at 298.15 K, from Surovy and Heinrich (*19*) at 298.15 K, and from light-scattering measurements (*1*) at 303.15 K.

system. Katayama, Sung, and Lightfoot (*7*) obtained total pressure values for this system but they reported possible errors in their analytical method. Their data, although scattered, are in agreement with those reported in this paper. Surovy and Heinrich (*19*) reported isothermal vapor–liquid measurements for this system at 298.15 K. These authors used a modified Brown still and were consequently able to measure vapor-phase mole fractions in addition to the equilibrium vapor pressures and liquid-phase mole fractions. A comparative plot showing excellent agreement between both sets of data of vapor-phase mole fraction against liquid-phase mole fraction at 298.15 K is given in Figure 2. Also included in Figure 2 are vapor–liquid equilibrium data calculated with the NRTL constants found by Ashcroft et al. (*1*) from Rayleigh light-scattering measurements for toluene–*n*-heptane at 303.15 K. Again agreement with our results is very good and is perhaps as close an agreement between Rayleigh light-scattering and vapor–liquid equilibrium data as has yet been published.

The good agreement between all three sets of data for the toluene–*n*-heptane system would suggest that the vapor–liquid equilibrium measurements and equation constants presented here for this system form a sound basis for process engineering design calculations. Any additional small uncertainty for systems containing sulfolane, due to the use of estimated critical constants for this compound, is likely to be minimal since the vapor-phase nonidealities would be expected to be small for these systems of low total pressure. The closeness to unity of the vapor-phase fugacity coefficients is evidence for this view.

Appendix

NRTL Equation

$$\frac{G^E}{RT} = x_1x_2\left[\frac{\tau_{21}\exp(-\alpha_{12}\tau_{21})}{x_1 + x_2\exp(-\alpha_{12}\tau_{21})} + \frac{\tau_{12}\exp(-\alpha_{12}\tau_{12})}{x_2 + x_1\exp(-\alpha_{12}\tau_{12})}\right]$$

$$\ln \gamma_1 = x_2^2\left[\frac{\tau_{12}\exp(-\alpha_{12}\tau_{12})}{(x_2 + x_1\exp(-\alpha_{12}\tau_{12}))^2} + \frac{\tau_{21}\exp(-2\alpha_{12}\tau_{21})}{(x_1 + x_2\exp(-\alpha_{12}\tau_{21}))^2}\right]$$

$$\ln \gamma_2 = x_1^2\left[\frac{\tau_{12}\exp(-2\alpha_{12}\tau_{12})}{(x_2 + x_1\exp(-\alpha_{12}\tau_{12}))^2} + \frac{\tau_{21}\exp(-\alpha_{12}\tau_{21})}{(x_1 + x_2\exp(-\alpha_{12}\tau_{21}))^2}\right]$$

where

$$\tau_{21} = (1/RT)(C_1 + D_1(273.15 - T))$$

$$\tau_{12} = (1/RT)(C_2 + D_2(273.15 - T))$$

$$\alpha_{12} = C_3 + D_3(273.15 - T)$$

Modified Wilson Equation

$$G^E/RT = -x_1 \ln (x_1 + x_2\Lambda_{21}) - x_2 \ln (x_1\Lambda_{12} + x_2) + x_1 \ln (x_1 + x_2\rho_{21}) + x_2 \ln (x_1\rho_{12} + x_2)$$

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

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

where

$$\rho_{12} = V_1^L/V_2^L$$

$$\rho_{21} = V_2^L/V_1^L$$

$$\Lambda_{21} = \rho_{21} \exp[-(1/RT)(C_1 + D_1(273.15 - T))]$$

$$\Lambda_{12} = \rho_{12} \exp[-(1/RT)(C_2 + D_2(273.15 - T))]$$

Glossary

C_1–C_3	constants of the NRTL or modified Wilson equations at 273.15 K
D_1–D_3	constants expressing the temperature dependence of the NRTL or modified Wilson constants
G	Gibbs function/J
G^E	excess Gibbs function/J mol^{-1}
R	gas constant = 8.3143 J K^{-1} mol^{-1}
T	temperature/K (IPTS 68)
T_c	critical temperature/K
P	pressure/N m^{-2}
P_i^0	vapor pressure of component i/N m^{-2}
P_c	critical pressure/N m^{-2}
V_i^L	molar volume of component i/m^3 mol^{-1}
V_c	critical volume/m^3 mol^{-1}
x_i	liquid-phase mole fraction of component i
y_i	vapor-phase mole fraction of component i

Greek Letters

α_{ij}	constant in NRTL equation
Λ_{ij}	constant in modified Wilson equation
η	vapor-phase association factor
μ	dipole moment/D
ρ_{ij}	constant in the modified Wilson equation = V_i^L/V_j^L
τ_{ij}	constant in the NRTL equation
ω	acentric factor
ω_H	acentric factor of homomorph

Literature Cited

(1) Ashcroft, S. J., Clayton, A. D., Shearn, R.B., unpublished data.
(2) Asselineau, L., Renon, H., *Chem. Eng. Sci.*, **25**, 1211 (1970).
(3) Casteel, J. F., Sears, P. G., *J. Chem. Eng. Data*, **19**, 196 (1974).
(4) Clayton, A. D., Ph.D. Thesis, University of Exeter, 1977.
(5) Engineering Sciences Data Unit, London, Physical Data, Chemical Engineering, Tables extant 1977.
(6) Hermsen, R. W., Prausnitz, J. M., *Chem. Eng. Sci.*, **18**, 485 (1963).
(7) Katayama, T., Sung, E. K., Lightfoot, E. N. *AIChE J.*, **11**, 924 (1965).
(8) O'Connell, J. P., Prausnitz, J. M., *Ind. Eng. Chem. Process Des. Develop.*, **6**, 245 (1967).
(9) Orye, R. V., Prausnitz, J. M., *Trans. Faraday Soc.*, **61**, 1338 (1965).
(10) Passut, C. A., Danner, R. P., *Ind. Eng. Chem. Process Des. Develop.*, **12**, 365 (1973).
(11) Powell, M. J. D., *Comput. J.*, **8**, 303 (1965) (Also Numerical Algorithms Group—NAG—Routine EO4FBF).
(12) Prausnitz, J. M., Eckert, C. A., Orye, R. V., O'Connell, J. P., "Computer Calculations for Multicomponent Vapor-liquid Equilibria", Prentice-Hall, Englewood Cliffs, N.J., 1965 Chapters 3 and 4.
(13) Reid, R. C., Sherwood, T. K., "Properties of Gases and Liquids", 2nd ed., McGraw-Hill, New York, 1966, pp 8–10.
(14) Renon, H., Ph.D. Thesis, University of California, Berkeley, 1966.
(15) Renon, H., Prausnitz, J. M., *AIChE J.*, **14**, 135 (1968).
(16) Sassa, Y., Konishi, R., Katayama, T., *J. Chem. Eng. Data*, **19**, 44 (1974).
(17) Shell Technical Bulletin, "Sulfolane", Shell Chemical Co., March 1964.
(18) Smith, B. D., Bowden, W. W., *Anal. Chem.*, **36**, 87 (1964).
(19) Surovy, J., Heinrich, J., *Sb. Pr. Chem. Fak. SVST*, 201 (1966); *Chem. Abstr.*, **66**, 69368*f* (1967).
(20) Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds", Vol. 2, Elsevier, Amsterdam, 1965, pp 13, 99.
(21) Tsuboka, T., Katayama, T., *J. Chem. Eng. Jpn.*, **8**, 181 (1975).

Received for review June 12, 1978. Accepted February 21, 1979.

Several Properties of the Dimethyl Sulfoxide–3-Methyl-2-oxazolidone System as Functions of Composition and Temperature

Michael D. Jackson and Paul G. Sears*

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506

Dielectric constants, viscosities, densities, and refractive indices for 11 binary mixtures of dimethyl sulfoxide and 3-methyl-2-oxazolidone were measured at 10 °C intervals within the range of 25–75 °C. The experimental data, excepting refractive indices, were fitted precisely to appropriate equations as separate functions of temperature and composition. Molar refractions also are discussed.

Introduction

The utility of dimethyl sulfoxide (Me_2SO) as an outstanding solvent for both electrolytes and nonelectrolytes has become well established and known during the last 2 decades. Studies in this laboratory within the last few years (*1*, *5*, *6*) have indicated that 3-methyl-2-oxazolidone (3Me2Ox), which has a dielectric constant essentially equal to that of water, similarly appears to have great potential as an electrolytic solvent. Me_2SO and 3Me2Ox have dielectric constants of 46.45 and 77.54 and viscosities of 1.991 and 2.450 cP, respectively, at 25 °C. Both Me_2SO and 3Me2Ox can be highly purified through a series of fractional freezings under nitrogen. The useful data reported herein concerning dielectric constants, viscosities, and other physical properties of Me_2SO–3Me2Ox mixtures were obtained in the course of systematic physicochemical investigations dealing with pure and mixed nonaqueous media.

0021-9568/79/1724-0199$01.00/0