the ether oxygens and the water molecules.

Schott (*6*) developed a relationship between the maximum deviation of fluidity and the hydration number of ether oxygens. He reported that the maximum number for the water–ether oxygen ratio in the smaller ethers in this series would be 2.03 ± 0.05. He postulated that, since two is the maximum number of water molecules that can be bound to each of the ether linkages by secondary valence forces, the excess water must be held in a different manner.

A regression analysis provided the functional relationship between viscosity and mole fraction:

$$1.0038 - 0.086435X - 0.028081X^2 + 0.10627X^3$$

where X is the mole fraction of ether. From this relationship the maximum deviation in the fluidity for tetraethylene glycol dimethyl ether occurred at a mole fraction of ether of 0.0815. This corresponded to a water–ether oxygen ratio of 2.254, with a deviation of 439% of predicted fluidity from observed fluidity. Wallace (*4*) reported that for triethylene glycol dimethyl ether the maximum deviation of fluidity occurs at a mole fraction of ether of 0.102, which corresponds to a water–ether oxygen ratio of 2.20, and a deviation of 354% of predicted fluidity from observed fluidity. It can be seen from these increasing water–ether oxygen ratios that there must be more than two water molecules for each ether linkage. Perhaps these excess water molecules are being trapped in the spaces within a particular arrangement of the ethers. This could be explained if the ethers were able to coil, or orient themselves in a spiral, much like a helix.

Registry No. Tetraethylene glycol dimethyl ether, 143-24-8.

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Vapor–Liquid Equilibria in Binary Systems Formed by Thiophene and Light Alcohols

Jaime O. Triday

Departamento de Procesos Químicos, Universidad Têcnica Federico Santa María, Valparaíso 110-V, Chile

Isothermal vapor pressure data over the whole range of composition were obtained for five binary systems: thiophene–methanol, thiophene–ethanol, thiophene–1-propanol, thiophene–2-propanol, and thiophene–1-butanol. Data for the first four systems were obtained at temperatures of 308.15, 313.15, and 318.15 K. For the last system, temperatures of 318.15, 328.15, and 338.15 K were used. Excess Gibbs energy equations suggested by Wilson and Renon–Prausnitz (NRTL) were used in the reduction of data. The Wilson equation gives a better fit than the NRTL equation for all these systems.

Introduction

Vapor–liquid phase equilibria measurements continue to be of major importance in thermodynamics, not only for their direct use in process design but also for their importance in the testing and extension of fluid mixture theories. As part of a program to investigate and to predict the phase equilibria in multicomponent systems, it became necessary to obtain vapor–liquid equilibrium data for a number of binary systems.

The aim of this work was to provide vapor–liquid isothermal equilibrium data for binary systems formed by thiophene and light alcohols.

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

Experimental Section

Table I. Physical Properties of the Pure Compounds at 293.15 K

	density/(g cm^{-3})		refractive index	
	obsd	lit.	obsd	lit.
thiophene	1.0639	1.064 4[b]	1.5290	1.528 7[b]
methanol	0.7911	0.791 31[a]	1.3290	1.328 40[a]
ethanol	0.7910	0.789 37[a]	1.3616	1.361 43[a]
1-propanol	0.8043	0.803 75[a]	1.3855	1.385 56[a]
2-propanol	0.7853	0.785 45[a]	1.3776	1.377 2[a]
1-butanol	0.8096	0.809 7[a]	1.3993	1.399 3[a]

[a] Reference *2*. [b] Reference *1*.

Materials. Analytical-grade reagents from Merck were used. Ethanol, 1-propanol, and 2-propanol were used without further purification, after gas chromatography failed to show any significant impurity. The certified minimum purities of these materials were 99.8%, 99.7%, and 99.7%, respectively. Thiophene, methanol, and 1-butanol were redistilled in a high-efficiency packed column. A heart cut was collected by discarding the first 20% distillate and the last 20% residue. The physical properties of these materials given in Tables I and II compare well with those reported in the literature (*1–3*).

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. The apparatus, which is described in detail by Vera (*4*), is shown schematically in Figure 1. It was in some respects similar to those used by several other authors: Renon (*5*), Hermsen (*6*), Orye (*7*), Harris (*8*), and Sassa (*9*). Briefly the major items were a large-diameter mercury manometer, measuring the difference in pressure between the reference high vacuum and measuring manifold systems, and a thermostatic bath containing the vapor pressure cell assembly. The latter consisted of a mercury null manometer connected to the static cell. Stirring of the contents

0021-9568/83/1728-0307$01.50/0

Table II. Vapor Pressures, P (kN m^{-2}), of the Pure Compounds

	thiophene		methanol		ethanol		1-propanol		2-propanol		1-butanol	
T/K	obsd	lit.	obsd	lit.	obsd	lit.	obsd	lit.	obsd	lit.	obsd	lit.
308.15	16.80	16.89^b	27.73	27.64^a	13.95	13.85^a	5.29	5.20^a	10.73	10.80^a		
313.15	20.80	20.73^b	35.17	35.09^a	18.07	18.00^a	6.91	6.99^a	14.18	14.23^a		
318.15	25.51	25.47^b	44.21	44.17^a	23.12	23.16^a	9.30	9.27^a	18.47	18.55^a	3.32	3.27^a
328.15	37.60	37.61^b									6.01	5.95^a
338.15	54.07	54.05^b									10.33	10.31^a

^{a} Reference 2. ^{b} Reference 3.

Table III. Isothermal Vapor-Liquid Equilibrium Data for Thiophene (1)-Alcohol (2)

	308.15 K		313.15 K		318.15 K	
x_1	y_1^{a}	P^b	y_1^{a}	P^b	y_1^{a}	P^b
Thiophene (1)-Methanol (2)						
0.000	0.000	27.73	0.000	35.17	0.000	44.21
0.083	0.199	32.55	0.195	41.18	0.199	51.28
0.185	0.305	34.81	0.299	43.97	0.291	54.60
0.290	0.360	36.00	0.353	45.04	0.345	55.66
0.394	0.392	36.00	0.385	45.04	0.376	55.66
0.520	0.417	35.74	0.410	44.64	0.401	55.27
0.605	0.430	35.47	0.423	44.24	0.415	54.73
0.690	0.441	35.21	0.434	43.84	0.427	54.07
0.790	0.456	34.54	0.452	42.91	0.446	53.01
0.855	0.472	33.21	0.471	41.45	0.468	50.88
0.900	0.493	32.15	0.496	39.72	0.497	48.49
0.935	0.527	30.69	0.536	37.60	0.542	45.57
0.945	0.544	29.76	0.555	36.27	0.562	43.97
0.950	0.554	29.23	0.567	35.87	0.575	43.18
0.961	0.583	28.56	0.600	34.67	0.610	41.18
1.000	1.000	16.80	1.000	20.80	1.000	25.51
Thiophene (1)-Ethanol (2)						
0.000	0.000	13.95	0.000	18.07	0.000	23.12
0.055	0.208	16.61	0.197	21.26	0.189	27.23
0.105	0.320	19.66	0.307	24.71	0.295	30.29
0.185	0.432	21.26	0.418	26.48	0.404	33.08
0.295	0.521	22.86	0.507	28.83	0.492	35.87
0.385	0.566	23.51	0.553	29.63	0.538	36.93
0.488	0.601	24.05	0.590	30.16	0.575	37.60
0.600	0.629	24.18	0.619	30.29	0.604	37.73
0.700	0.648	24.05	0.639	30.16	0.625	37.46
0.804	0.664	23.91	0.657	30.02	0.645	37.07
0.855	0.672	23.78	0.667	29.89	0.658	36.53
0.898	0.681	23.65	0.678	29.32	0.674	36.00
0.917	0.687	23.51	0.686	29.23	0.684	35.87
0.942	0.699	23.38	0.702	28.96	0.707	35.07
0.983	0.776	21.79	0.794	26.57	0.817	31.35
1.000	1.000	16.80	1.000	20.80	1.000	25.51
Thiophene (1)-1-Propanol						
0.000	0.000	5.29	0.000	6.91	0.000	9.30
0.016	0.164	6.51	0.158	8.50	0.139	10.89
0.031	0.271	7.31	0.263	9.43	0.235	12.22
0.074	0.457	9.17	0.446	11.69	0.410	14.75
0.095	0.513	9.83	0.502	12.49	0.466	15.81
0.146	0.604	11.69	0.592	14.75	0.559	18.47
0.195	0.659	13.29	0.647	16.47	0.616	20.46
0.289	0.722	15.01	0.710	18.86	0.685	23.26
0.391	0.762	16.21	0.750	20.46	0.729	25.11
0.474	0.783	17.27	0.772	21.52	0.753	26.44
0.601	0.807	17.80	0.796	22.19	0.781	27.10
0.680	0.819	17.93	0.809	22.32	0.796	27.50
0.774	0.833	18.33	0.825	22.58	0.815	27.90
0.847	0.847	18.47	0.843	22.72	0.835	28.03
0.875	0.855	18.60	0.853	22.98	0.846	28.30
0.945	0.892	18.33	0.897	22.72	0.894	27.90
1.000	1.000	16.80	1.000	20.80	1.000	25.51
Thiophene (1)-2-Propanol						
0.000	0.000	10.73	0.000	14.18	0.000	18.47
0.022	0.122	11.93	0.110	15.41	0.104	19.79
0.043	0.209	13.02	0.190	16.87	0.181	21.52
0.081	0.322	14.75	0.297	18.73	0.285	23.65
0.097	0.358	15.28	0.332	19.40	0.320	24.44
0.195	0.499	18.07	0.473	22.72	0.460	28.43
0.294	0.575	19.66	0.551	24.71	0.538	30.82
0.372	0.613	20.46	0.591	25.51	0.579	31.88
0.483	0.650	20.99	0.632	26.04	0.620	32.42
0.590	0.676	21.26	0.660	26.57	0.649	32.81
0.690	0.696	21.39	0.683	26.84	0.673	32.95
0.735	0.704	21.52	0.693	27.10	0.683	33.35
0.825	0.724	21.26	0.719	26.44	0.710	32.68
0.939	0.786	20.46	0.796	25.24	0.790	31.08
0.980	0.876	19.53	0.891	23.51	0.888	28.96
1.000	1.000	16.80	1.000	20.80	1.000	25.51
Thiophene (1)-1-Butanol (2)						
0.000	0.000	3.32	0.000	6.01	0.000	10.33
0.100	0.713	10.89	0.634	16.21	0.586	23.91
0.184	0.811	14.88	0.754	22.05	0.715	31.88
0.280	0.859	18.47	0.816	27.10	0.786	38.93
0.401	0.889	20.99	0.857	31.22	0.833	44.11
0.513	0.905	22.58	0.880	33.74	0.860	47.95
0.597	0.914	23.65	0.892	35.07	0.875	50.22
0.689	0.921	25.24	0.903	36.67	0.888	52.74
0.791	0.929	25.64	0.913	38.26	0.902	54.47
0.871	0.936	26.30	0.923	38.93	0.916	55.66
0.895	0.939	26.44	0.927	39.06	0.922	55.93
0.927	0.945	26.70	0.935	39.59	0.933	56.99
0.943	0.950	26.84	0.941	39.86	0.940	57.52
0.967	0.961	26.57	0.954	39.59	0.957	56.73
1.000	1.000	25.51	1.000	37.60	1.000	54.07

^{a} Calculated from the Wilson equation. ^{b} Units: kN m^{-2}.

of the cell was achieved with a small PTFE-coated magnet activated by a magnetic stirrer motor sited under the bath. The mercury levels were read by using an Eberbach cathetometer.

The binary mixtures were sealed in a separate still for degassing. The air was removed by freezing the mixture with liquid nitrogen and opening the still to the vacuum system. Afterward, the mixture was melted under vigorous agitation by the magnetic stirrer. Degassing was considered complete when the vacuum gage located in the vacuum line did not detect any air at the time of opening the still with the frozen mixture. The mixture was transferred to the equilibrium cell by distilling from the still and condensing in the cell with liquid nitrogen. The cell was then gradually warmed and thermostated at the desired temperature. The small null manometer was balanced by bleeding dry air into its reference side through a needle valve. The mixture in the cell was under continuous agitation to assure uniform temperature and composition. After the vapor pressure measuring at three different temperatures, the sample was completely transferred from the equilibrium cell to the still previously evacuated and cooled with liquid nitrogen.

Mixture compositions were determined from refractive index measurements using a Baush and Lomb Abbe-3L refractometer thermostated at 20 °C. Calibration plots of index of refraction vs. composition were prepared for each binary system.

Considering the effect of interpolation on the index of refraction calibration curve to find the sample composition in ±0.001 mole fraction, the accuracy in temperature of ±0.05 °C, and a maximum error of 0.2 mmHg in measuring the

Table IV. Critical Properties (*12*) and Parameters Characterizing Vapor-Phase Nonideality (*13*)

	P_c/atm	T_c/K	V_c/(cm^3 mol^{-1})	ω	a	b
thiophene	56.2	580.2	233.9	0.205	0	0
methanol	78.5	513.2	118.0	0.572	0.0878	0.0560
ethanol	63.0	516.0	167.0	0.635	0.0878	0.0572
1-propanol	51.0	540.7	218.0	0.612	0.0878	0.0447
2-propanol	47.0	508.2	247.6	0.667	0.0878	0.0537
1-butanol	43.6	563.0	274.6	0.590	0.0878	0.0367

pressure, the experimental vapor pressures are accurate to better than 0.1 kN m^{-2} at each temperature.

The experimental results are given in Table III.

Results and Discussion

The binary vapor pressure data were fitted to the Wilson equation (*10*) and the NRTL equation of Renon and Prausnitz (*11*)

Wilson equation

$$-G^E/RT = x_1 \ln (x_1 + x_2\Lambda_{12}) + x_2 \ln (x_2 + x_1\Lambda_{21}) \quad (1)$$

where

$$\Lambda_{ij} \equiv (v_j^L/v_i^L) \exp\{-(\lambda_{ij} - \lambda_{ii})/RT\} \quad (2)$$

λ_{ij} are physical parameters for the i–j pair interaction in the binary mixture

NRTL equation

$$\frac{G^E}{RT} = x_1x_2\left(\frac{\tau_{21}G_{21}}{x_1 + x_2G_{21}} + \frac{\tau_{12}G_{12}}{x_2 + x_1G_{12}}\right) \quad (3)$$

where

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \quad (4)$$

$$\tau_{ij} = (g_{ij} = g_{jj})/RT \quad (5)$$

g_{ij} and α_{ij} are physical parameters for the i–j pair interaction in the binary mixture.

The technique used for data fitting was basically that described by Prausnitz et al. (*12*). Vapor-phase nonidealities were determined from the virial equation truncated after the second term. The second virial coefficients were calculated from the generalized correlations presented by Tsonopoulos (*13*). The critical properties and other parameters required for estimating the second virial coefficients by the correlation of Tsonopoulous are listed in Table IV. Pure-component molar volumes were taken from ref *12* and are reported in Table V.

Before data reduction, the smoothness of the equilibrium data was tested by using the spline fit technique described by Klaus and Van Ness (*14*). The smoothed equilibrium data obtained were practically identical with the raw data. The raw data were used in the reduction of data.

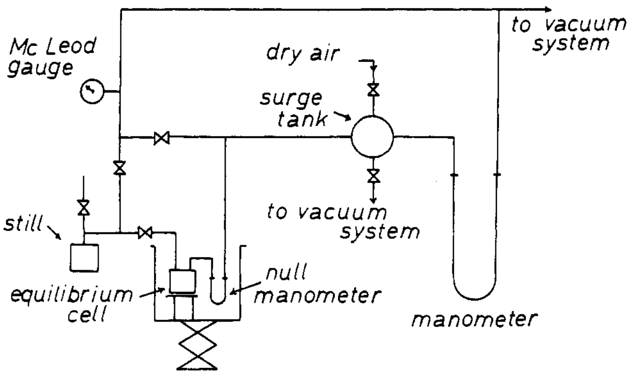

Figure 1. Schematic view of the apparatus.

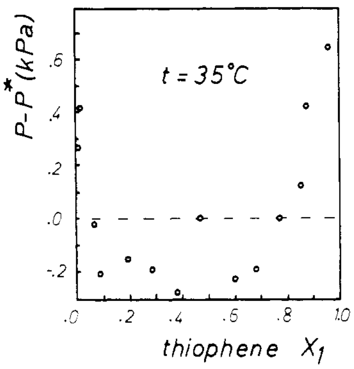

Figure 2. Residuals of pressures vs. liquid mole fraction for the system thiophene (1)–2-propanol (2) at 35 °C.

By means of a nonlinear regression routine, the physical parameters were obtained by minimizing the objective function

$$S = \sum_i^N \left(\frac{P - P^*}{P}\right)^2 \times 100 \quad (6)$$

where P and P^* are respectively the experimental and calculated values of the total vapor pressure and N is the total number of experimental points.

All the regression analyses were carried out by using double precision arithmatic upon a DEC-2020 computer.

The α_{ij} parameter of the NRTL equation did not improve the goodness of fit of the data and was taken as 0.47, according with the recommendations given by Renon (*11*).

The physical parameters determined from the regression analyses are given in Table VI. The Wilson equation gives a better fit than the NRTL for all these systems. Even though, by analysis of scatter graphs of $P - P^*$ vs. x_1 systematic deviations were obtained for these systems. Figure 2 shows this behavior for the system thiophene (1)–2-propanol (2) at 308.15 K when the Wilson equation was used.

Systematic deviations between P and P^* calculated mean that y values are in error, simply because of the inadequacy of the correlating equation.

Table V. Temperature Dependence of Liquid Molar Volume (*12*)

	T_1	v_1	T_2	v_2	T_3/K	v_3/(cm^3 mol^{-1})
thiophene	293.15	79.049	313.15	80.865	333.15	82.799
methanol	273.15	39.559	373.15	44.874	473.15	59.939
ethanol	273.15	57.141	323.15	60.356	373.15	64.371
1-propanol	293.15	74.785	343.15	78.962	393.15	84.515
2-propanol	298.15	76.982	328.15	79.806	407.75	91.007
1-butanol	273.15	89.873	298.15	91.995	307.75	92.812

Table VI. Constants of the Wilson and NRTL Equations

temp/K	$(\lambda_{12} - \lambda_{11})$/(J mol^{-1})	$(\lambda_{12} - \lambda_{22})$/(J mol^{-1})	SD^a	$(g_{12} - g_{11})^b$/(J mol^{-1})	$(g_{12} - g_{22})^b$/(J mol^{-1})	SD^a
Thiophene (1)-Methanol (2)						
308.15	611	7954	0.74	2602	5515	1.46
313.15	661	7615	0.68	2598	5351	1.31
318.15	674	7398	0.41	2611	5184	0.97
Thiophene (1)-Ethanol (2)						
308.15	473	9209	1.69	1686	6468	2.85
313.15	431	8678	1.46	1623	6238	2.48
318.15	469	7900	0.74	1598	5933	1.64
Thiophene (1)-1-Propanol (2)						
308.15	1138	5665	1.54	1540	4799	1.72
313.15	1264	5134	1.70	1456	4489	1.79
318.15	1155	5013	1.25	1485	4402	1.38
Thiophene (1)-2-Propanol (2)						
308.15	1264	6029	1.28	1640	5050	1.73
313.15	1205	5414	0.90	1502	4724	1.23
318.15	1197	5444	1.05	1523	4682	1.38
Thiophene (1)-1-Butanol (2)						
318.15	1331	6155	2.28	1276	5597	2.84
328.15	1029	6272	1.90	971	5456	2.44
338.15	996	5515	2.05	866	5071	2.45

[a] The standard deviation of the fit = $100\{\Sigma_1^N[(P - P^*)/P]^2/(N - m)\}^{1/2}$, where m is the number of equation constants fitted and N is the total number of experimental points. [b] The α_{12} parameter was taken as 0.47.

Table VII. Azeotropic Pressures and Compositions

T/K	P/(kN m^{-2})	$x_1 = y_1$
Thiophene (1)-Methanol (2)		
308.15	36.01	0.342
313.15	45.06	0.343
318.15	55.68	0.342
Thiophene (1)-Ethanol (2)		
308.15	24.19	0.644
313.15	30.30	0.644
318.15	37.75	0.608
Thiophene (1)-1-Propanol (2)		
308.15	18.67	0.915
313.15	23.19	0.931
318.15	28.48	0.923
Thiophene (1)-2-Propanol (2)		
308.15	21.56	0.780
313.15	27.17	0.772
318.15	33.51	0.786
Thiophene (1)-1-Butanol (2)		
318.15	26.86	0.953
328.15	39.99	0.959
338.15	57.64	0.955

Finally, azeotropic pressures and compositions derived from the fitted data are reported in Table VII.

Acknowledgment

I thank Dr. F. Aguirre for his valuable advise on the Experimental Section. R. Lopez, R. Inostroza, and F. Romero performed the experimental measurements.

Glossary

a, b	constants of Tsonopoulos's correlation
G^E	excess Gibbs function, J mol^{-1}
G_{ij}, g_{ij}	constants of the NRTL equation
P	pressure, kN m^{-2}
P_c	critical pressure, atm
R	gas constant = 8.314 J K^{-1} mol^{-1}
T	temperature, K
T_c	critical temperature, K
v_i^L	molar volume of component i, cm^3 mol^{-1}
v_c	critical molar volume, cm^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}, λ_{ij}	constant in Wilson equation
τ_{ij}	constant in NRTL equation
ω	acentric factor

Registry No. Methanol, 67-56-1; ethanol, 64-17-5; 1-propanol, 71-23-8; 2-propanol, 67-63-0; 1-butanol, 71-36-3; thiophene, 110-02-1.

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