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Vapor−Liquid Equilibria for Methanol + Tetraethylene Glycol Dimethyl Ether

X. Esteve, S. K. Chaudhari,[†] and A. Coronas[*]

Department of Electrical and Mechanical Engineering, Universitat Rovira i Virgili, Cra de Salou s/n,
43006 Tarragona, Spain

Vapor−liquid equilibrium ($P-T-x$) for the methanol + tetraethylene glycol dimethyl ether binary system were obtained by the static method in the range of temperatures from 293.15 to 423.15 K at 10 K intervals. The modified vapor pressure apparatus used is described. The Kuczynsky method was used to calculate the liquid and vapor composition and the activity coefficients of methanol from the initial composition of the sample and the measured pressure and temperature. The results were correlated by the NRTL and UNIQUAC temperature dependent activity coefficient models. This system shows nearly ideal behavior at 323.15 K, but positive deviations from ideality at lower temperatures and negative deviations at higher temperatures are observed. The activity coefficients become more negative with the increase in temperature and mole fraction of methanol. The excess molar enthalpy using the Gibss−Helmholtz equation and the NRTL and UNIQUAC parameters were calculated at 303.15 K and compared with experimental data.

Introduction

There is a growing interest in heat-driven heat pump systems for upgrading waste heat to useful higher temperature levels. The classical ammonia + water and water + lithium bromide binary systems used in absorption refrigeration have considerable disadvantages at higher temperatures. For ammonia + water the operating pressures have to be higher, and for water + lithium bromide there are corrosion and crystallization problems. Therefore, organic mixtures such as tetraethylene glycol dimethyl ether (TEGDME or 2,5,8,11,14-pentaoxapentadecane or E181) with 2,2,2-trifluoroethanol (Bockelmann and Renz, 1983; Seher and Stephan, 1983; Stephan and Hengerer, 1993) and polyethylene glycol 250 dimethyl ether, TEGDME, or glycerol with methanol (Stüven, 1989; Boer et al., 1994; Boer, 1995) have been suggested. Methanol + TEGDME might be a promising working pair for high-temperature heat pump applications. In order to characterize the performance of this working pair, reliable vapor pressure data are needed over a wide temperature and composition range. Therefore, vapor−liquid equilibrium (VLE) for this binary system has been obtained by a static method in the temperature range of 293.15−423.15 K at 10 K intervals and pressures up to 1000 kPa.

Kuczynski et al. (1986) have reported VLE for this system in the temperature range of 423 and 503 K, whereas Khosla et al. (1991) have obtained some data ($x_1 < 0.2$) between 473 and 513 K. Activity coefficients at infinite dilution of methanol in TEGDME have been measured using gas−liquid chromatography by Schiller and Gmehling (1992) in the temperature range between 343 and 393 K.

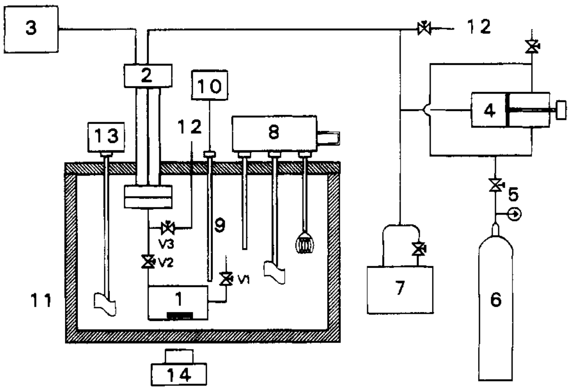

Figure 1. Schematic drawing of the static vapor pressure apparatus: (1) stainless steel cell; (2) diaphragm type differential pressure transducer (DTP) (Ruska 2439−702); (3) differential pressure null indicator; (4) pressure controller (Ruska 3891−801); (5) pressure gauge (Bourdom type); (6) nitrogen cylinder; (7) digital pressure gauge (Ruska 6242); (8) thermoregulator; (9) platinum resistance thermometer (Anton Paar); (10) temperature indicator; (11) thermostat bath (with Basylon M20 oil); (12) to vaccum pump; (13) bath stirrer; (14) magnetic driver of the cell stirrer.

Experimental Section

Materials. Methanol (Fluka, >99.8%) was purified by refluxing a large volume and subsequent fractional distillation. It was stored over type 4A molecular sieves. Before use it was degassed by several freezing, evacuating, and thawing cycles until the density remained constant. Tetraethylene glycol dimethyl ether (Aldrich, 99+%) was used with no further purification, but it was thoroughly degassed by refluxing under vacuum and was stored under vacuum. The purity of the chemicals was verified by measuring their densities at 298.15 K in a vibrating tube densimeter (Anton Paar, DMA 602/60) and then comparing them with those in the literature (Riddick and Bunger, 1986; Trejo et al., 1991).

Apparatus. The total vapor pressures of the binary mixtures were measured by a static method (Pemberton and Mash, 1978; Chaudhari et al., 1995). The apparatus is schematically shown in Figure 1. It consists of the equilibrium cell and pressure and temperature control and measuring systems.

The sample cell was modified so that the mixture was continuouosly stirred. The liquid sample contained in a stainless steel cell was separated from the pressure measuring system by a differential pressure null transducer (DPT) (Ruska Model 2439-702). Three bellows valves (Nupro SS-4BG) were used to connect the equilibrium cell to the DPT and vacuum line. Valve V1 was used for

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[*] To whom correspondence should be addressed.

[†] On leave from the National Chemical Laboratory, Pune, India.

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loading the pure components, V2 for isolating the cell from the DPT while degassing, and V3 for evacuation. The cell was connected to the lower end of the DPT.

For the pressure measurements, a digital pressure gauge (Ruska Model 6242) with two ranges of 0−150 and 0−1000 kPa with a resolution of ±1 Pa was connected to the top side of the DPT in series with a precise pressure controller (Ruska Model 3891-801). The overall reproducibility of the pressure measurement is better than ±0.1 kPa.

A double-walled thermostat bath with a 25 L capacity filled with silicon oil (Basylon M20) was used. The temperature in the bath was controlled by a Haake proportional controller to better than ±0.01 K up to 373.15 K and ±0.02 above 373.15 K. The temperature was measured very near the cell with a Pt100 platinum resistance thermometer (Anton Paar, MKT 100). A Mettler electronic balance with an accuracy of ±0.1 mg was used for weighing the pure components.

Procedure. Estimating the Cell Volume. In order to calculate the amount of substance present in the vapor phase, the total volume of the cell and the connecting lines between the DPT and valves V1−V3 (V2 open) should be known. This volume was calculated by filling the cell with pure nitrogen gas at about 10 bar of pressure and expanding the gas in a cylinder of known volume (150 cm^3) at a constant temperature of 293.15 K. Initial and final pressures were measured by applying nitrogen gas to the top of the DPT to obtain a null. The volume of the cylinder was accurately obtained by filling it with degassed water at 293.15 K and then weighing it. The total volume of the cell (V_{cell}) was calculated from the relation

$$V_{\text{cell}}P_{\text{initial}} = (V_{\text{cell}} + V_{\text{cylinder}})P_{\text{final}} \qquad (1)$$

Triplicate measurement gave a value of (48.26 ± 0.05) cm^3.

Loading the Sample. The required amount of each pure component was taken separately in a cylindrical glass vessel having a Teflon stopcock, degassed, weighed, and transferred under vacuum to the cell through valve V1 by connecting the glass vessel to the valve by a special Viton O-ring. Initially, TEGDME was loaded by heating the glass vessel and condensing it in the cell whose bottom was cooled with liquid nitrogen. Then methanol was similarly transferred by evaporating and totally condensing, and the glass vessels were again weighed. The mixture in the cell was stirred and again degassed to remove the traces of air.

Measuring the Vapor Pressure. After the known amounts of degassed pure liquids were added to the cell, a plug was installed on valve V1 to prevent contamination and leakage. Then the cell and the lower part of the DPT were lowered into the thermostat. The vapor pressure of each mixture was first measured at 293.15 K. The pressure of the sample was balanced by applying nitrogen gas to the top of the DPT and adjusting the pressure by the pressure controller to give a zero null indication. The liquid in the cell was continuously stirred by a magnetic needle encapsulated in a stainless steel tube which was driven from the outside via magnetic coupling by a variable speed electric motor. After equilibrium was reached the constant pressure was measured on a digital gauge. Then the temperature was raised successively from 293.15 to 423.15 K at 10 K intervals.

Next, a small quantity of methanol was added to the cell contents to get a new higher mole fraction, and the above procedure was repeated. This was done until enough vapor space was left over the liquid. Then a new composition was again loaded, and pressure, temperature, and total composition (P−T−x) data were obtained over the entire mole fraction range. The actual liquid mole fractions of methanol x_1 and vapor mole fractions y_1 at each temperature were calculated taking into account the amounts present in the vapor phase using the method given by Kuczynski et al. (1986). The vapor pressure correlation from Reid et al.(1988) for methanol and our correlation (Chaudhari et al., 1995) for TEGDME were used. The Peng−Robinson equation of state (Peng and Robinson, 1976) was used to calculate the molar vapor volume of methanol. The critical pressure and temperature and the acentric factor for methanol have been taken from Reid et al.'s (1988) property data bank. To calculate the liquid molar volumes, density values for methanol and TEGDME were obtained from the density−temperature correlations (Smith et al., 1986; Coronas et al., 1995). The thermal expansion of the cell was taken into account while calculating the liquid mole fraction. The excess molar volumes have a negligible effect on the mole fraction calculation. The activity coefficient of methanol in the liquid phase, γ_1, was calculated using the relation

$$Py_1\phi_1(P,T) = P_1^\circ x_1\phi_1(P_1^\circ,T)\gamma_1 \exp\left[\frac{v_{1,l}^\circ(P - P_1^\circ)}{RT}\right] \qquad (2)$$

where P is the total pressure, y_1 and x_1 are the vapor and liquid mole fractions of methanol, P_1^0 is the vapor pressure of methanol, R is the gas constant, $v_{1,l}^\circ$ is the molar volume in the liquid phase, and $\phi_1(P,T)$ and $\phi_1(P^\circ,T)$ are the fugacity coefficients at the total pressure and at the saturated vapor pressure, respectively. The fugacity coefficients can be calculated from the Peng−Robinson equation (Peng and Robinson, 1976).

Initially, the apparatus was tested by measuring the vapor pressure of methanol from 293.15 to 403.15 K and comparing the results with the values obtained from the Wagner equation with the parameters of Reid et al.'s property data bank (Reid et al., 1988). The measured values match those calculated to within ±0.05%. The experimental data and the discrepancies are specified in Table 1.

Results and Correlation

The vapor−liquid equilibrium data obtained for methanol + TEGDME are given in Table 2. The P−T−x_1 data were correlated by temperature dependent five-parameter NRTL and four-parameter UNIQUAC equations, as follows:

NRTL

$$\ln \gamma_i = x_j^{\,2}\left[\tau_{ji}\left(\frac{G_{ji}}{x_i + x_jG_{ji}}\right)^2 + \frac{\tau_{ij}G_{ij}}{(x_j + x_iG_{ij})^2}\right]$$

$$\tau_{ij} = C_{ij}/RT$$

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

$$C_{ij} = C_{ij}^{\ \text{c}} + C_{ij}^{\ \text{T}}(T - 273.15)$$

UNIQUAC

$$\ln \gamma_i = \ln\frac{\phi_i}{x_i} + \frac{z}{2}q_i \ln\frac{\theta_i}{\phi_i} + \phi_j\left(l_i - \frac{r_i}{r_j}l_j\right) - q'_i \ln(\theta'_i + \theta'_j\,\tau_{ji}) + \theta'_jq'_i\left(\frac{\tau_{ji}}{\theta'_i + \theta'_j\tau_{ji}} - \frac{\tau_{ij}}{\theta'_j + \theta'_i\tau_{ij}}\right)$$

$$\phi_i = \frac{x_ir_i}{x_ir_i + x_jr_j};\quad \theta_i = \frac{x_iq_i}{x_iq_i + x_jq_j};\quad \theta'_i = \frac{x_iq'_i}{x_iq'_i + x_jq'_j}$$

$$\tau_{ij} = \exp(-\,C_{ij}/RT);\quad C_{ij} = C_{ij}^{\ \text{C}} + C_{ij}^{\ \text{T}}(T - 273.15)$$

Table 1. Comparison of Experimental Vapor Pressures of Methanol with Those Calculated from the Wagner Equation with the Parameters of Reid et al.'s (1988) Property Data Bank (ΔP = P(this work) − P(lit.))

T/K	P/kPa	ΔP/kPa	T/K	P/kPa	ΔP/kPa	T/K	P/kPa	ΔP/kPa	T/K	P/kPa	ΔP/kPa
293.15	13.02	0.00	323.15	55.60	−0.03	353.15	181.10	0.01	383.15	480.40	−0.02
303.15	21.90	0.01	333.15	84.65	0.00	363.15	255.75	−0.01	393.15	641.10	−0.02
313.15	35.50	0.02	343.15	125.40	0.04	373.15	353.80	−0.05	403.15	842.20	0.01

Table 2. Experimental Results and Calculated Activity Coefficients for Methanol (1) + TEGDME (2)

P/kPa	x_1	y_1	γ_1	P/kPa	x_1	y_1	γ_1	P/kPa	x_1	y_1	γ_1
	T = 293.15 K				T = 343.15 K				T = 393.15 K		
1.31	0.0881	1.0000	1.146	10.35	0.0877	0.9988	0.960	45.01	0.0867	0.9910	0.870
2.31	0.1600	1.0000	1.113	18.82	0.1594	0.9994	0.960	82.22	0.1579	0.9955	0.873
3.33	0.2377	1.0000	1.079	28.05	0.2371	0.9996	0.961	123.85	0.2353	0.9973	0.879
4.33	0.3157	1.0000	1.056	37.59	0.3151	0.9998	0.967	168.38	0.3132	0.9982	0.894
5.37	0.3997	1.0000	1.034	47.99	0.3990	0.9998	0.973	218.16	0.3973	0.9988	0.907
6.40	0.4793	1.0000	1.028	57.77	0.4787	0.9999	0.975	267.58	0.4773	0.9992	0.921
7.45	0.5658	1.0000	1.013	68.18	0.5654	0.9999	0.972	324.75	0.5645	0.9994	0.938
8.18	0.6244	1.0000	1.007	75.55	0.6235	0.9999	0.976	362.64	0.6200	0.9996	0.949
9.45	0.7232	1.0000	1.005	88.38	0.7226	1.0000	0.982	432.30	0.7207	0.9997	0.965
10.42	0.7988	1.0000	1.003	98.30	0.7985	1.0000	0.987	488.80	0.7977	0.9998	0.978
11.59	0.8843	1.0000	1.007	109.25	0.8837	1.0000	0.989	550.61	0.8817	0.9999	0.989
12.42	0.9603	1.0000	0.993	119.40	0.9603	1.0000	0.993	608.50	0.9603	1.0000	0.996
	T = 303.15 K				T = 353.15 K				T = 403.15 K		
2.06	0.0881	0.9999	1.074	14.50	0.0876	0.9980	0.939	57.06	0.0864	0.9878	0.856
3.68	0.1599	1.0000	1.056	26.40	0.1592	0.9990	0.940	104.20	0.1575	0.9939	0.858
5.42	0.2377	1.0000	1.046	39.46	0.2369	0.9994	0.942	157.55	0.2348	0.9963	0.867
7.13	0.3156	1.0000	1.036	53.00	0.3148	0.9996	0.950	214.51	0.3126	0.9976	0.881
8.96	0.3995	1.0000	1.028	67.93	0.3988	0.9997	0.959	278.77	0.3968	0.9984	0.896
10.70	0.4792	1.0000	1.023	81.82	0.4786	0.9998	0.960	343.57	0.4769	0.9989	0.912
12.40	0.5658	1.0000	1.004	97.51	0.5653	0.9999	0.966	418.13	0.5642	0.9992	0.930
13.65	0.6244	1.0000	1.001	107.98	0.6231	0.9999	0.969	468.20	0.6188	0.9994	0.944
15.82	0.7231	1.0000	1.001	126.60	0.7224	0.9999	0.977	560.20	0.7201	0.9996	0.960
17.50	0.7988	1.0000	1.002	141.54	0.7984	1.0000	0.986	636.80	0.7974	0.9998	0.976
19.37	0.8842	1.0000	1.001	157.59	0.8835	1.0000	0.989	718.53	0.8809	0.9999	0.987
20.95	0.9603	1.0000	0.997	172.60	0.9603	1.0000	0.994	801.50	0.9602	1.0000	1.000
	T = 313.15 K				T = 363.15 K				T = 413.15 K		
3.20	0.0880	0.9998	1.033	19.83	0.0874	0.9970	0.918	71.20	0.0861	0.9839	0.842
5.81	0.1598	0.9999	1.032	36.16	0.1590	0.9985	0.920	130.11	0.1570	0.9919	0.846
8.60	0.2376	0.9999	1.027	54.29	0.2366	0.9991	0.926	197.00	0.2342	0.9952	0.855
11.30	0.3155	1.0000	1.015	72.98	0.3145	0.9994	0.934	269.04	0.3120	0.9969	0.871
14.38	0.3994	1.0000	1.020	93.79	0.3985	0.9996	0.944	350.30	0.3962	0.9979	0.885
17.13	0.4791	1.0000	1.012	113.72	0.4783	0.9997	0.951	433.93	0.4764	0.9985	0.904
19.68	0.5656	1.0000	0.984	136.27	0.5651	0.9998	0.961	530.80	0.5639	0.9990	0.924
21.96	0.6242	1.0000	0.995	150.87	0.6225	0.9998	0.964	594.90	0.6174	0.9992	0.940
25.42	0.7230	1.0000	0.993	177.49	0.7221	0.9999	0.973	715.90	0.7193	0.9995	0.957
28.04	0.7988	1.0000	0.991	199.03	0.7983	0.9999	0.984	816.80	0.7971	0.9997	0.974
31.08	0.8841	1.0000	0.992	221.93	0.8832	1.0000	0.988	924.39	0.8799	0.9999	0.986
33.84	0.9603	1.0000	0.994	244.00	0.9603	1.0000	0.997	1033.0	0.9602	1.0000	0.997
	T = 323.15 K				T = 373.15 K				T = 423.15 K		
4.87	0.0879	0.9996	1.006	26.58	0.0872	0.9955	0.902	87.72	0.0857	0.9791	0.832
8.85	0.1597	0.9998	1.006	48.50	0.1587	0.9977	0.904	160.26	0.1564	0.9895	0.836
13.11	0.2375	0.9999	1.002	72.77	0.2362	0.9986	0.908	243.10	0.2335	0.9938	0.845
17.43	0.3154	0.9999	1.002	98.38	0.3141	0.9991	0.921	332.30	0.3113	0.9960	0.861
22.15	0.3993	0.9999	1.004	126.79	0.3982	0.9994	0.931	434.67	0.3955	0.9973	0.878
26.38	0.4790	1.0000	0.996	154.42	0.4780	0.9996	0.942	539.75	0.4759	0.9981	0.896
30.77	0.5656	1.0000	0.983	185.66	0.5649	0.9997	0.954	663.26	0.5636	0.9988	0.919
34.12	0.6240	1.0000	0.987	206.18	0.6218	0.9998	0.960	744.80	0.6158	0.9990	0.936
39.61	0.7229	1.0000	0.988	243.60	0.7217	0.9999	0.972	900.70	0.7184	0.9994	0.954
43.93	0.7987	1.0000	0.991	273.46	0.7981	0.9999	0.980	1033.0	0.7967	0.9996	0.973
49.07	0.8840	1.0000	0.999	306.34	0.8828	1.0000	0.990				
52.93	0.9603	1.0000	0.991	337.80	0.9603	1.0000	0.998				
	T = 333.15 K				T = 383.15 K						
7.18	0.0878	0.9993	0.980	34.91	0.0870	0.9935	0.885				
13.08	0.1596	0.9996	0.982	63.74	0.1583	0.9967	0.888				
19.46	0.2373	0.9998	0.981	95.88	0.2358	0.9980	0.893				
25.96	0.3153	0.9799	0.984	129.86	0.3137	0.9987	0.906				
33.08	0.3992	0.9999	0.989	168.12	0.3977	0.9991	0.921				
39.72	0.4789	0.9999	0.989	205.20	0.4777	0.9994	0.931				
46.36	0.5655	0.9999	0.976	247.85	0.5647	0.9996	0.946				
51.48	0.6238	0.9999	0.981	276.02	0.6210	0.9997	0.954				
60.00	0.7228	1.0000	0.985	327.70	0.7213	0.9998	0.968				
66.51	0.7986	1.0000	0.987	368.95	0.7979	0.9999	0.980				
74.05	0.8839	1.0000	0.989	414.53	0.8823	0.9999	0.989				
80.60	0.9603	1.0000	0.992	456.30	0.9603	1.0000	0.995				

Table 3. Parameters of NRTL and UNIQUAC Equations for the Methanol + TEGDME System

	C_{12}^{C}/ (J·mol^{-1})	C_{12}^{T}/ (J·mol^{-1}·K^{-1})	C_{21}^{C}/ (J·mol^{-1})	C_{21}^{T}/ (J·mol^{-1}·K^{-1})	α_{12}
NRTL	515.4	−4.71	−50.7	−3.50	6.24
UNIQUAC	−1075.9	−2.05	3554.1	−0.30	

Table 4. Root Mean Square Deviations and the Variance of the Fit for Methanol + TEGDME Using NRTL and UNIQUAC Equations

	RMSD(*P*)/kPa	RMSD(*T*)/K	RMSD(x_1)	*s*
NRTL	0.16	0.02	0.0007	5.84
UNIQUAC	0.08	0.01	0.0006	2.84

where $i = 1, j = 2$, or $i = 2, j = 1$. The fugacity coefficients and the Poynting factor corrections for TEGDME have been neglected.

The parameters are fitted using the maximum likelihood principle (Prausnitz et al., 1980) in order to minimize the function

$$s = \sum_{i}^{N}\left(\frac{(P^{\text{calc}} - P^{\text{meas}})_i^{\,2}}{\sigma_{P_i}^{\,2}} + \frac{(T^{\text{calc}} - T^{\text{meas}})_i^{\,2}}{\sigma_{T_i}^{\,2}} + \frac{(x^{\text{calc}} - x^{\text{meas}})_i^{\,2}}{\sigma_{x_i}^{\,2}}\right)$$

where *P* is the pressure, *T* the temperature, and *x*, the mole fraction of methanol. The standard deviations for *P*, *T* and *x* are taken as 0.1 kPa, 0.02 K, and 0.0005, respectively.

The values of the volume parameter *r* and the surface area parameters *q* and *q′* needed in the UNIQUAC equation for methanol were taken from Prausnitz et al. (1980) and for TEGDME from Trejo et al. (1991). The fitting parameters and root mean square deviations in *P*, *T*, and x_1 are given in Tables 3 and 4, respectively.

The experimental vapor pressure data for all the isotherms are plotted in Figure 2 along with the data calculated using the NRTL equation for comparison. The agreement is excellent.

We attempted to calculate the excess molar enthalpy from the vapor pressure data using the Gibbs−Helmholtz equation and the NRTL and UNIQUAC parameters. The calculated and experimental H^E values at 303.15 K (Esteve et al., 1995) are plotted in Figure 3 for comparison.

Discussion

The vapor pressure data indicate that this binary system shows nearly ideal behavior at 323.15 K whereas positive deviations at lower temperatures and negative deviations at higher temperatures are observed. The ln γ values become more negative with the increase in temperature and mole fraction of methanol.

We compared the vapor pressures of methanol + TEGDME at 423.15 K with Kuczynski et al.'s values. Their values deviate up to 6% positively above $x_1 > 0.5$ compared to ours. At lower mole fractions their values deviate more. We found that their activity coefficients at 423.15 K and $x_1 < 0.5$ are not consistent with their higher temperature data. The deviation may be due to inadequate degassing of TEGDME which gives rise to apparent higher pressures due to dissolved air. The deviation of the activity coefficients at infinite dilution calculated from the NRTL parameters and those of Schiller and Gmehling (1992) is between 5.5% and 14%, the calculated values always being higher.

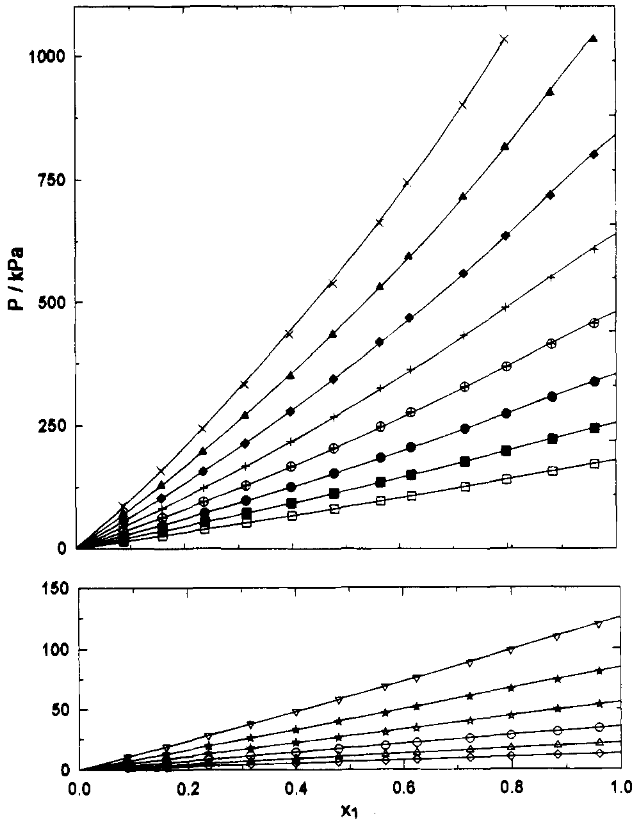

Figure 2. Experimental and calculated vapor pressure data of the methanol + TEGDME system as a function of the mole fraction of methanol at different temperatures: ◇, 293.15 K; △, 303.15 K; ○, 313.15 K; ☆, 323.15 K; ★, 333.15 K; ▽, 343.15 K; □, 353.15 K; ■, 363.15 K; ●, 373.15 K; ⊕, 383.15; +, 393.15 K; ◆, 403.15 K; ▲, 413.15 K; ×, 423.15 K; −, calculated by using the NRTL equation.

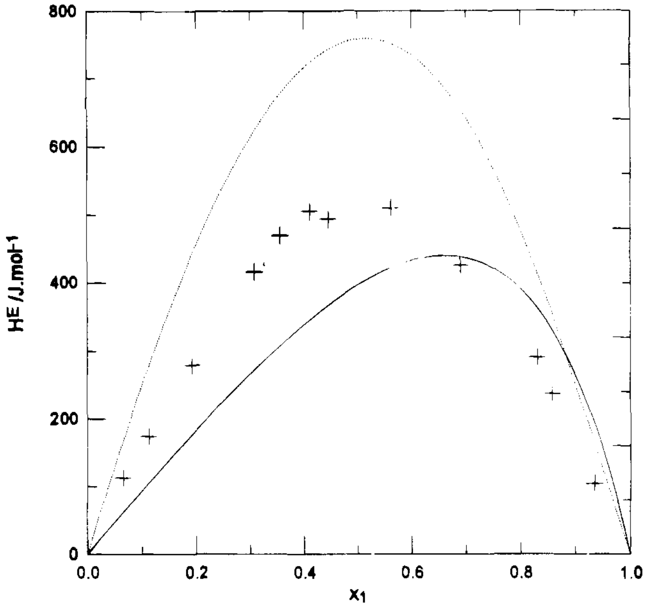

Figure 3. Experimental (+) and calculated from VLE, using NRTL (−) and UNIQUAC (···) equations, excess molar enthalpy data for methanol + TEGDME at 303.15 K as a function of the mole fraction of methanol.

The excess molar enthalpy at 303.15 K is positive in the whole range of composition, having a maximum of about 500 J·mol^{-1} at $x_1 = 0.5$. The agreement between experimental and predicted data is reasonably good for NRTL. The predicted values from UNIQUAC are always higher with a maximum deviation of 250 J·mol^{-1} at $x_1 = 0.5$.

Conclusion

The VLE data are obtained for methanol + TEGDME between 293.15 and 423.15 K over the entire composition range. The NRTL and UNIQUAC temperature dependent equations fit the results satisfactorily. The experimental and calculated, from NRTL, excess enthalpies at 303.15 K compare reasonably well.

This binary system shows more negative deviations at higher temperatures which may be good for the operation of high-temperature absorption heat pumps using this working pair.

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