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Densities, Viscosities, and Enthalpies of Mixing of the Binary System Methanol + Polyethylene Glycol 250 Dimethyl Ether at 303.15 K

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Densities, kinematic viscosities, and excess molar enthalpies have been determined for methanol + polyethylene glycol 250 dimethyl ether at 303.15 K over the entire range of composition and at atmospheric pressure. Experimental viscosities were correlated by the McAllister, Stephan, Soliman, and Marshall correlations.

Introduction

Research on new working fluid pairs for use in absorption refrigeration systems and heat transformers continues. The selection of a suitable substance can be made by a systematic study of its physical and thermodynamic properties. The NH_3 + H_2O and H_2O + LiBr working pairs are well known in refrigeration technology. But these show important disadvantages due to higher temperature levels of the heat transformer process. The NH_3 + H_2O pair works between 80 and 150 °C and at pressures to 64 bar. For H_2O + LiBr there are problems of corrosion and crystallization which can be reduced only by the addition of inhibitors. Therefore, organic mixtures as the absorbent like polyethylene glycol dimethyl ether with other polar organic molecules (working fluids) have been suggested (*1*). The vapor pressures of methanol + polyethylene glycol 250 dimethyl ether (PEGDME250) have been published over a wide range of temperature (*2*). However, additional physical and thermodynamic measurements are not available in the literature.

This work reports the measurement of density, viscosity, and excess molar enthalpy for the system methanol + PEGDME 250 at 303.15 K. The excess molar volumes were calculated from the density results. The viscosity data were correlated by the method of McAllister (*3*), Stephan (*4*), and Soliman and Marshall (*5, 6*).

Experimental Section

Materials. Methanol (Fluka, >99.8%) was purified by refluxing a large volume for several days and fractional distillation. Then it was degassed by several freezing and thawing cycles under vacuum until the density remained constant and then stored over molecular sieves type 4A. PEGDME 250 (Fluka) was used without further purification but kept over molecular sieves for several days before use. The purities of the chemicals were verified by the measurement of the density and viscosity at 298.15 and 303.15 K and are in agreement with literature values (*7, 8*).

Apparatus. Densities of the liquids and liquid mixtures were measured using a densimeter (Anton Paar DMA602H-DMA60) at 303.15 K. The vibrating-tube temperature was regulated to better than ±0.01 K using a Julabo F20 thermostat together with a digital precision thermometer (Anton Paar MKT100). Immediately prior to each series of measurements, water and air were used to calibrate the densimeter. Binary mixtures were prepared by using a Mettler AE260 balance. The possible error in the mole fractions is estimated to be less than ±0.0001, and the precision of the measured densities is estimated to be higher than $\pm 2 \times 10^{-5}$ $g\cdot cm^{-3}$.

Kinematic viscosities of the pure liquids and their mixtures were measured with a (AVS 300) Schott viscometer, consisting of a basic control unit, a measuring stand, a thermostat, and a calibrated Ubbelohde suspended level viscometer. The viscometer was recalibrated using benzene and *n*-heptane. Hagenbach correction was applied for the Ubbelohde viscometer supplied by Schott-Geräte. Time measurements were made automatically between two measuring levels due to the change in light intensity which is converted to a digital electrical signal to start the internal crystal-controlled clock with readout display. The electronic timer is capable of measuring time to within ±0.01 s. The temperature was kept constant within ±0.01 K. The estimated error in the kinematic viscosity was $\pm 5 \times 10^{-4}$ $mm^2\cdot s^{-1}$.

The excess molar enthalpies were measured using a heat flux Calvet-type microcalorimeter (Setaram C-80) at 303.15 K. Calibration of the calorimeter was done by use of water + methanol at 298.15 K. The internal consistency of the results of this calibration was within ±1.0%. The results were compared with the literature (*9*) and agreed within ±1.0%.

Result and Correlation

The experimental values of densities, kinematic viscosities, dynamic viscosities, excess molar volumes, and excess molar enthalpies for the methanol + polyethylene glycol 250 dimethyl ether at 303.15 K are presented in Tables 1 and 2.

Excess molar volumes were calculated from

$$V^E = \frac{x_1M_1 + x_2M_2}{\varrho} - \frac{x_1M_1}{\varrho_1} - \frac{x_2M_2}{\varrho_2} \qquad (1)$$

where x_1 and x_2 are the mole fractions, M_1 and M_2 are the molecular masses, and ϱ, ϱ_1, and ϱ_2 are the densities of the mixture, component 1, and component 2, respectively. The molecular formula for the PEGDME 250 is $CH_3O(CH_2CH_2O)_nCH_3$ where n = 3–9. In all calculations the molecular weight of PEGDME 250 is taken as 283.33.

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Table 1. Data on the Density (ϱ), Kinematic Viscosity (ν), Dynamic Viscosity (η), and Excess Volume (V^E) for Methanol (1) + Polyethylene Glycol 250 Dimethyl Ether (2) at 303.15 K

x_1	$\varrho/(\mathrm{g{\cdot}cm^{-3}})$	$\nu/(\mathrm{mm^2{\cdot}s^{-1}})$	$\eta/(\mathrm{mPa{\cdot}s})$	$V^E/(\mathrm{cm^3{\cdot}mol^{-1}})$
0.0000	1.026 17	5.3495	5.4895	
0.0300	1.025 31	5.2532	5.3862	−0.0670
0.0413	1.025 02	5.2541	5.3856	−0.1042
0.0815	1.023 72	5.0950	5.2159	−0.1814
0.1318	1.022 01	4.9248	5.0332	−0.2922
0.1859	1.019 96	4.7686	4.8638	−0.4082
0.2150	1.018 75	4.6761	4.7638	−0.4682
0.2592	1.016 73	4.5385	4.6144	−0.5523
0.2891	1.015 27	4.4379	4.5057	−0.6138
0.3363	1.012 66	4.2774	4.3316	−0.6932
0.3891	1.009 47	4.0918	4.1305	−0.8013
0.4373	1.005 87	3.9218	3.9448	−0.8515
0.4456	1.005 28	3.8869	3.9074	−0.8734
0.5168	0.998 81	3.5871	3.5828	−0.9409
0.5313	0.997 35	3.5168	3.5075	−0.9599
0.5498	0.995 30	3.4294	3.4133	−0.9714
0.5862	0.990 95	3.2479	3.2185	−1.0027
0.6442	0.982 58	2.9438	2.8925	−1.0289
0.6994	0.972 52	2.6374	2.5649	−1.0340
0.7454	0.961 96	2.3392	2.2502	−1.0200
0.7963	0.946 93	2.0196	1.9124	−0.9749
0.8619	0.919 25	1.5815	1.4538	−0.8362
0.8997	0.896 58	1.3308	1.1932	−0.7067
0.9291	0.873 74	1.1268	0.9845	−0.5803
0.9552	0.847 32	0.9519	0.8066	−0.4046
0.9724	0.826 00	0.8312	0.6866	−0.2740
0.9884	0.802 27	0.7203	0.5779	−0.1278
1.0000	0.782 03	0.6487	0.5073	

Table 2. Excess Molar Enthalpies (H^E) for Methanol (1) + Polyethylene Glycol 250 Dimethyl Ether (2) at 303.15 K

x_1	$H^E/(\mathrm{J{\cdot}mol^{-1}})$	x_1	$H^E/(\mathrm{J{\cdot}mol^{-1}})$
0.0403	67.0	0.5498	587.0
0.0857	147.3	0.5675	586.6
0.1252	206.7	0.6242	568.8
0.1538	249.4	0.6539	563.8
0.1814	287.6	0.6924	534.2
0.2003	315.1	0.7544	486.7
0.2506	378.8	0.8037	411.5
0.2954	433.0	0.8477	352.9
0.3528	490.6	0.8913	265.1
0.4078	525.7	0.9413	136.2
0.4404	545.8	0.9529	112.7
0.4882	572.1		

Excess molar properties having asymmetrical composition dependence are difficult to fit to the Redlich–Kister equation. We found that for V^E the best fits were obtained by Ott et al. (*10*), who include an exponential switching factor:

$$V^E/(\mathrm{cm^3{\cdot}mol^{-1}}) = x_1x_2[\exp(-\alpha x_1)\sum_{i=0}^{1}A_i(1-2x_1)^i + (1-\exp(-\alpha x_1))\sum_{i=0}^{3}B_i(1-2x_1)^i \quad (2)$$

The parameters A_i, B_i, and α calculated by unweighted least squares using a Marquard algorithm are shown in Table 3, together with the standard deviations s.

In the case of H^E, the following Redlich–Kister equation gave the best correlation:

$$H^E/(\mathrm{J{\cdot}mol^{-}1}) = x_1x_2\sum_{i=1}^{n}a_i(x_2-x_1)^{i-1} \quad (3)$$

where the coefficients a_i have been determined by a linear least-squares fitting procedure. The values of the parameters a_i and the standard deviations s are listed in Table 3.

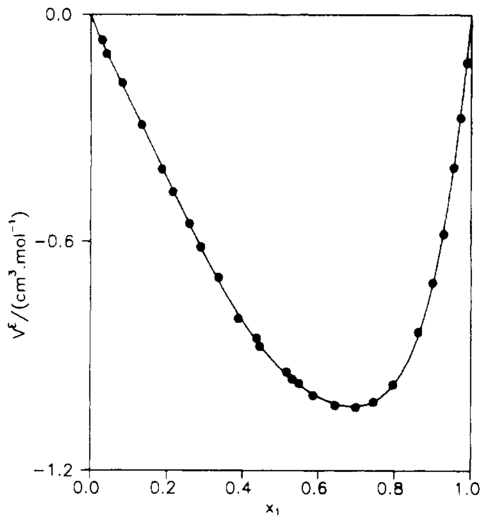

Figure 1. Excess molar volumes V^E at 303.15 K for methanol (1) + polyethylene glycol 250 dimethyl ether (2).

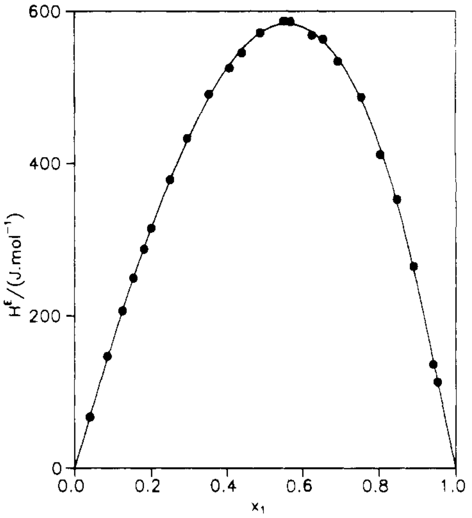

Figure 2. Excess molar enthalpies H^E at 303.15 K for methanol (1) + polyethylene glycol 250 dimethyl ether (2).

The composition dependence of the kinematic viscosity was correlated by the following equations:

(i) McAllister two-parameter equation (*3*)

$$\ln[\gamma_m M_m] = x_1^3\ln[\gamma_1 M_1] + x_2^3\ln[\gamma_2 M_2] + 3x_1^2x_2\ln[\gamma_{12}M_{12}] + 3x_2^2x_1\ln[\gamma_{21}M_{21}] \quad (4)$$

$$M_m = x_1M_1 + x_2M_2;\quad M_{12} = \frac{2M_1+M_2}{3};\quad M_{21} = \frac{2M_2+M_1}{3}$$

where γ_{12} and γ_{21} are the fitted parameters.

(ii) McAllister three-parameter equation (*3*)

$$\ln[\gamma_m M_m] = x_1^4\ln[\gamma_1 M_1] + x_2^4\ln[\gamma_2 M_2] + 4x_1^3x_2\ln[\gamma_{1112}M_{1112}] + 6x_1^2x_2^2\ln[\gamma_{1122}M_{1122}] + 4x_1x_2^3\ln[\gamma_{2221}M_{2221}] \quad (5)$$

$$M_m = x_1M_1 + x_2M_2;\quad M_{1112} = \frac{3M_1+M_2}{4}$$

$$M_{1122} = \frac{M_1+M_2}{2};\quad M_{2221} = \frac{M_1+3M_2}{4}$$

Table 3. Parameters and Standard Deviations (*s*) for Methanol (1) + Polyethylene Glycol 250 Dimethyl Ether (2) at 303.15 K

Parameters of Eq 2								
system	α	A_0	A_1	B_0	B_1	B_2	B_3	*s*
V^E	0.650 87	−2.390 64	−0.219 40	−7.193 12	3.632 07	−1.804 10	7.536 87	0.0062

Parameters of Eq 3					
system	a_0	a_1	a_2	a_3	*s*
H^E	2304.7	−612.5	−31.4	169.3	5.1

Table 4. Comparison of the Values of the Standard Deviation for Soliman, Stephan, and McAllister's Equations of Viscosities at 303.15 K

	$\sigma/(10^{-6}\ \mathrm{m^2 \cdot s^{-1}})$			
system	Soliman	Stephan	McAllister two-param	McAllister three-param
methanol (1) + PEGDME 250 (2)	0.035	0.83	0.23	0.11

Coefficients of the Soliman Correlation

system	γ_{12}	B_{12}	concn range
methanol (1) + PEGDME 250 (2)	0.135 91	3.894 41	0.0300−0.9884

In this case γ_{1112}, γ_{1122}, and γ_{2221} are the three adjustable parameters.

(iii) Stephan equation (*4*)

$$\ln \gamma_m = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 + \ln[1 + x_1x_2/(A + Bx_2^2)] \quad (6)$$

where *A* and *B* are the fitted parameters.

(iv) Soliman and Marshall (*5*, *6*)

$$\ln \gamma_m = x_1^3 \ln \gamma_1 + x_2^3 \ln \gamma_2 + 3x_1x_2 \ln \gamma_{12} + \frac{B_{12}x_1x_2}{(M_1/M_2)^2x_1 + x_2} \quad (7)$$

where M_1 and M_2 are the molecular weights of the compounds and γ_{12} and B_{12} the adjustable parameters.

For the four correlations, the parameters were determined from experimental data using a nonlinear least-squares fit. Table 4 shows the standard deviations for the studied systems. In all the cases the best correlations were found with the Soliman and Marshall equation, and the coefficients are given in Table 4.

Discussion

Figures 1 and 2 show the experimental values of excess properties V^E and H^E as a function of the mole fraction of component 1. The continuous curves were calculated from eqs 2 and 3 using the coefficients given in Table 3.

Excess molar volumes are negative, and the excess enthalpies are positive. This can be explained in terms of positive contributions due to breaking of like interactions of the pure liquids and negative contributions due to the formation of unlike interactions and the packing effect. In the present study the negative V^E is mainly due to the close packing effect and the intermolecular interactions. Since PEGDME 250 is bulkier in size, it may be accommodating methanol molecules in the voids. The positive H^E may be due to the hydrogen bond breaking between methanol molecules by PEGDME 250.

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