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Isothermal and Isobaric Vapor−Liquid Equilibria of the Ternary System of 2,2-Dimethoxypropane + Acetone + Methanol

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The isothermal ($T = 323.15$ K) and the isobaric ($P = 66.66$ kPa and 79.99 kPa) vapor−liquid equilibria (VLE) for the ternary system of 2,2-dimethoxypropane + acetone + methanol were measured with an inclined ebulliometer. The measured results for the ternary system are compared with the calculated ones from the UNIQUAC equation using only temperature-dependent binary parameters obtained from the binary literature values and resulted in satisfactory results. The ternary VLE data are useful in the design of efficient separation process of 2,2-dimethoxypropane, acetone, and methanol.

Introduction

2,2-Dimethoxypropane (DMP, CAS Registry No. 77-76-9), a leuco transparent liquid with a strong odor is one of the important intermediates of vitamin synthesis.[1] Recently, the condensation of acetone and methanol is one of the main routes for industrial production of 2,2-dimethoxypropane and 2-methoxypropene. During the process of 2,2-dimethoxypropane and 2-methoxypropene production, a reliable knowledge of the vapor−liquid equilibria (VLE) behavior is a prerequisite for the separation of DMP, acetone, and methanol. The isobaric VLE for 2,2-dimethoxypropane with methanol and for 2,2-dimethoxypropane with acetone at $P = 99.99$ kPa are reported by Brunner and Scholz.[2] The binary azeotropic data of 2,2-dimethoxypropane with methanol and of 2,2-dimethoxypropane with acetone determined under atmospheric and enhanced pressures are provided by Tao et al.[3] Recently, our group has also published the binary isothermal and isobaric VLE data for 2,2-dimethoxypropane with methanol and for 2,2-dimethoxypropane with acetone.[4] The isothermal and isobaric VLE data for acetone with methanol are available in the literatures.[5−7] But we have not found the ternary VLE data of DMP + acetone + methanol in the literature. However, a knowledge of this ternary VLE data is important and indispensable in the design of the more efficient separation processes. In addition, it can be used to test and develop models for correlation and prediction of thermodynamic properties of mixtures.

In this paper, the ternary isothermal and isobaric VLE data for the ternary system DMP + acetone + methanol at a temperature of 323.15 K and pressures of 66.66 kPa and 79.99 kPa are reported. The measured ternary results are compared with those calculated from the UNIQUAC equation using temperature-dependent binary parameters, which were obtained from the binary literature data for the binary system of acetone + methanol at $T = 298.15$ K,[5] 313.15 K,[6] 323.15 K,[6] and 328.15 K;[7] for DMP + acetone at $T = 318.15$ K,[4] 328.15 K,[4] and at $P = 40.00$ kPa,[4] 66.66 kPa,[4] and 99.99 kPa;[4] and for DMP + methanol at $T =$ 318.15 K,[4] 328.15 K,[4] and at $P = 66.66$ kPa,[4] 79.99 kPa,[4] and 99.99 kPa.[4] The temperature-dependent binary parameters are reported too.

Table 1. Physical Properties of the Pure Compounds

	d (293.15 K)		n_D (293.15 K)		T_b (101.325 kPa)	
	g·cm^{-3}				K	
compound	exptl	lit	exptl	lit	exptl	lit
DMP	0.8402	0.8400[8]	1.3780	1.3780[8]	352.95	356.15[8] 352.41[5] 351.50[7]
acetone	0.7846	0.7845[8]	1.3589	1.3588[8]	329.18	329.20[8]
methanol	0.7865	0.7866[8]	1.3289	1.3288[8]	337.72	337.75[8]

Experimental Section

The DMP (highest commercial grade, Zhejiang JB Co., Ltd.), acetone, and methanol (analytical reagent grade, Shanghai Chemical Co.) were fractionally distilled using a 150 cm high column. The purities of the materials were checked in our laboratory by gas chromatography, and the values obtained are > 0.998 mass fraction (GC) for all the compounds. The physical properties of the pure materials are listed in Table 1 along with literature values.[5,7,8] Densities of the pure materials and mixtures were measured with an Anton Paar DMA 602 densimeter, with an estimated total uncertainty of 0.00001 g·cm^{-3}. Refractive indices were measured with an Abbe type refractometer (WZS-I model, made in Shanghai) with a precision of ± 0.0001.

The isothermal and isobaric VLE measurements were done by using the inclined ebulliometer apparatus with a pump-like stirrer as described elsewhere.[9−12] The ebulliometric method is based on the overall concentration (x^0) instead of the equilibrium concentration (x) in the liquid phase. The ebulliometer was connected to a pressure controlling system. The temperature inside the ebulliometer was measured with a standard platinum resistance thermometer connected to a digital multimeter (Keithley 195A) with sensitivity of 0.01 K. The accuracy of the temperature was estimated to be 0.05 K. The pressure was indirectly measured by measuring the boiling temperature of pure water in a separate ebulliometer as described elsewhere.[9] The estimated uncertainty of the indirect pressure measurements was 150 Pa. All mixtures were weighed by analytical balance and prepared by mass. The uncertainty on the composition measurements was estimated to be 0.0001 mole fraction. The detailed procedure has been described elsewhere.[9−11]

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Table 2. Antoine Coefficients *A*, *B*, and *C* for Equation 3

compound	*A*	*B*	*C*
DMP	4.97568	670.371	−127.62
acetone	6.25760	1219.97	−42.50
methanol	7.20587	1582.27	−33.42

Theory Section

At equilibrium between the liquid phase and the vapor phase:

$$Py_i\phi_i = P_i^{\mathrm{S}}\phi_i^{\mathrm{S}}x_i\gamma_i \exp[v_i^{\mathrm{L}}(P_i - P_i^{\mathrm{S}})/RT] \tag{1}$$

where P is the total pressure, y_i is the vapor mole fraction of component i, and ϕ_i is the fugacity coefficient of component i, calculated from virial equation:

$$\ln \phi_i = (2\sum_j y_jB_{ij} - \sum_i \sum_j y_iy_jB_{ij})P/RT \tag{2}$$

where the second virial coefficients for pure substances (B_{ii}) and the cross-coefficient (B_{ij}) were calculated according to the method of Hayden and O'Connel.[13] x_i is the liquid mole fraction of component i, and v_i^{L} is the pure liquid molar volume calculated from the modified Rackett equation.[14] The P_i^{S}/kPa is the saturated vapor pressure and can be calculated from the Antoine equation:

$$\log(P_i^{\mathrm{S}}) = A - B/(C + T) \tag{3}$$

where T is in K.

For acetone and methanol, the constants *A*, *B*, and *C* given in Dechema Chemistry Data Series[15] were used and

Table 3. Correlation Results for Binary Systems and Root-Mean-Square Deviations for $\delta P/P$ and δT/K, $T_r = T/T_0$

systems	a_{12}/K	a_{21}/K	$10^2\ \delta P/P$	δT/K	lit
DMP (1) + acetone (2)	$209.08 + 88.15T_r$	$152.46 - 294.26T_r$	0.985	0.27	4
DMP (1) + methanol (2)	$673.80 + 73.22T_r$	$303.13 - 407.55T_r$	0.989	0.25	4
acetone (1) + methanol (2)	$388.81 - 58.18T_r$	$109.17 - 206.05T_r$	0.847	0.22	5−7

Table 4. Experimental and Calculated Results for DMP (1) + Acetone (2) + Methanol (3) at T = 323.15 K, Where P Is Pressure and $\delta P/P$[a] Is the Deviation in Pressure

x_1	x_2	y_1 [b]	y_2 [b]	γ_1	γ_2	γ_3	P_{exp}/kPa	P_{cal}/kPa	$10^2\ \delta P/P$
0.1242	0.1231	0.1457	0.2001	2.2276	1.3291	1.0531	68.82	69.29	−0.68
0.2503	0.3748	0.1835	0.4478	1.5298	1.0705	1.3084	76.04	76.91	−1.15
0.3749	0.2494	0.2674	0.3246	1.4063	1.1058	1.3676	71.85	72.62	−1.07
0.4984	0.2499	0.3245	0.3435	1.2392	1.1288	1.6049	69.23	69.85	−0.89
0.1248	0.6598	0.0846	0.7003	1.5225	1.0186	1.4277	81.16	81.53	−0.45
0.1278	0.3834	0.1055	0.4681	1.7609	1.1163	1.1852	77.67	78.56	−1.14
0.2506	0.4995	0.1702	0.5653	1.4470	1.0337	1.4364	77.50	78.30	−1.03
0.2499	0.1252	0.2343	0.1845	1.7920	1.2144	1.1355	69.83	70.79	−1.37
0.3751	0.3717	0.2492	0.4558	1.3414	1.0648	1.5016	73.87	74.99	−1.51
0.5100	0.3677	0.3200	0.4970	1.1951	1.1091	1.8214	69.18	69.75	−0.82
0.1383	0.7422	0.0902	0.7799	1.4628	1.0062	1.5508	80.52	80.43	0.11
0.1250	0.2537	0.1201	0.3498	1.9561	1.2054	1.1074	74.11	74.93	−1.10
0.2500	0.6239	0.1620	0.6907	1.3889	1.0162	1.5962	77.53	77.93	−0.51
0.2458	0.2629	0.1989	0.3394	1.6382	1.1239	1.2139	74.32	75.70	−1.86
0.3745	0.4994	0.2386	0.5979	1.2948	1.0450	1.6809	73.99	74.80	−1.10
0.4960	0.1303	0.3465	0.1925	1.2926	1.1811	1.4601	67.59	68.47	−1.30
0.7494	0.1250	0.4886	0.2432	1.0612	1.3718	2.2245	58.06	58.04	0.04
0.6249	0.1250	0.4067	0.2040	1.1505	1.2483	1.7606	63.76	63.82	−0.09
0.6241	0.2499	0.3924	0.3898	1.1234	1.2038	1.9747	64.55	64.74	−0.30
									0.98

[a] $\delta P/P = (P_{\mathrm{exp}} - P_{\mathrm{cal}})/P_{\mathrm{exp}}$. [b] y_1 and y_2 are calculated values.

Table 5. Experimental and Calculated Results for DMP (1) + Acetone (2) + Methanol (3) at P = 66.66 kPa, Where δT[a]/K Is the Deviation in Temperature

x_1	x_2	y_1[b]	y_2[b]	γ_1	γ_2	γ_3	T_{exp}/K	T_{cal}/K	δT/K
0.1242	0.1231	0.1462	0.2010	2.2437	1.3335	1.0536	322.28	322.04	0.24
0.2503	0.3748	0.1843	0.4519	1.5551	1.0766	1.3182	319.65	319.31	0.34
0.3749	0.2494	0.2674	0.3271	1.4147	1.1119	1.3740	321.07	320.68	0.39
0.4984	0.2499	0.3240	0.3447	1.2415	1.1323	1.6101	322.10	321.82	0.28
0.1248	0.6598	0.0856	0.7034	1.5798	1.0208	1.4522	318.08	318.12	−0.04
0.1278	0.3834	0.1070	0.4736	1.8104	1.1231	1.1919	319.27	319.06	0.21
0.2506	0.4995	0.1707	0.5688	1.4755	1.0381	1.4537	319.24	319.08	0.16
0.2499	0.1252	0.2349	0.1855	1.8014	1.2192	1.1370	322.00	321.68	0.32
0.3751	0.3717	0.2487	0.4587	1.3526	1.0704	1.5138	320.47	320.13	0.34
0.5100	0.3677	0.3193	0.4980	1.1974	1.1118	1.8292	322.18	322.00	0.18
0.1383	0.7422	0.0911	0.7813	1.5160	1.0075	1.5842	318.20	318.36	−0.16
0.1250	0.2537	0.1215	0.3538	1.9953	1.2132	1.1100	320.48	320.24	0.24
0.2500	0.6239	0.1621	0.6925	1.4184	1.0191	1.6232	319.21	319.22	−0.01
0.2458	0.2629	0.1999	0.3428	1.6590	1.1310	1.2189	320.42	320.03	0.39
0.3745	0.4994	0.2378	0.6001	1.3071	1.0491	1.7005	320.43	320.26	0.17
0.4960	0.1303	0.3465	0.1925	1.2931	1.1820	1.4608	322.83	322.53	0.30
0.7494	0.1250	0.4940	0.2372	1.0593	1.3424	2.1789	326.72	326.77	−0.05
0.6249	0.1250	0.4077	0.2023	1.1491	1.2407	1.7522	324.28	324.21	0.07
0.6241	0.2499	0.3936	0.3882	1.1222	1.1992	1.9655	323.95	323.78	0.17
									0.25

[a] $\delta T = T_{\mathrm{exp}} - T_{\mathrm{cal}}$. [b] y_1 and y_2 are calculated values.

Table 6. Experimental and Calculated Results for DMP (1) + Acetone (2) + Methanol (3) at P = 79.99 kPa, Where δT^{a}/K Is the Deviation in Temperature

x_1	x_2	$y_1{}^b$	$y_2{}^b$	γ_1	γ_2	γ_3	T_{exp}/K	T_{cal}/K	δT/K
0.1242	0.1231	0.1418	0.1947	2.1669	1.3125	1.0511	327.03	326.91	0.12
0.2503	0.3748	0.1831	0.4457	1.5191	1.0679	1.3043	324.50	324.18	0.32
0.3749	0.2494	0.2673	0.3202	1.3929	1.0961	1.3574	326.04	325.77	0.27
0.4984	0.2499	0.3265	0.3374	1.2290	1.1131	1.5812	327.06	326.79	0.27
0.1248	0.6598	0.0846	0.7004	1.5280	1.0188	1.4301	322.77	322.66	0.11
0.1278	0.3834	0.1050	0.4666	1.7513	1.1150	1.1838	323.91	323.59	0.32
0.2506	0.4995	0.1701	0.5643	1.4404	1.0327	1.4324	323.98	323.67	0.31
0.2499	0.1252	0.2313	0.1799	1.7610	1.1986	1.1307	326.58	326.15	0.43
0.3751	0.3717	0.2496	0.4527	1.3307	1.0595	1.4898	325.26	324.78	0.48
0.5100	0.3677	0.3232	0.4915	1.1846	1.0966	1.7856	327.07	326.69	0.38
0.1383	0.7422	0.0902	0.7800	1.4673	1.0063	1.5537	322.97	323.00	−0.03
0.1250	0.2537	0.1187	0.3461	1.9286	1.1999	1.1055	325.06	324.70	0.36
0.2500	0.6239	0.1619	0.6902	1.3834	1.0156	1.5911	323.98	323.81	0.17
0.2458	0.2629	0.1979	0.3359	1.6207	1.1180	1.2096	325.02	324.46	0.56
0.3745	0.4994	0.2392	0.5959	1.2844	1.0414	1.6643	325.23	324.83	0.40
0.4960	0.1303	0.3472	0.1864	1.2807	1.1557	1.4399	327.35	326.74	0.61
0.7494	0.1250	0.5011	0.2291	1.0565	1.3011	2.1142	331.41	330.99	0.42
0.6249	0.1250	0.4111	0.1956	1.1428	1.2082	1.7158	329.06	328.81	0.25
0.6241	0.2499	0.3996	0.3799	1.1153	1.1741	1.9140	328.73	328.21	0.52
									0.38

[a] $\delta T = T_{\text{exp}} - T_{\text{cal}}$. [b] y_1 and y_2 are calculated values.

are shown in Table 2. For DMP, the constants provided by Jiang et al.[4] were used and are also shown in Table 2.

The liquid-phase activity coefficient (γ_i) was calculated from the UNIQUAC equation[16] with the temperature-dependent binary parameters. The pure component structural parameters for each component are as follows: for DMP, $\gamma = 4.31$, $q = q' = 3.87$; for acetone, $\gamma = 2.57$, $q = q' = 2.34$; for methanol, $\gamma = 1.43$, $q = 1.43$, $q' = 0.96$. The temperature-dependent parameter of a_{ij} is as follows:

$$a_{ij} = a_{ij}{}^{(0)} + a_{ij}{}^{(1)}T_{\text{r}} \tag{4}$$

where $T_{\text{r}} = T/T_0$. T_0 is an arbitrarily chosen reference temperature, in this case 315.00 K. To obtain the temperature-dependent parameters, a nonlinear optimization method was used to minimize the objective function:

$$J = \sum_j (P - P_{\text{exp}})_j{}^2/P_{\text{exp},j}{}^2 + \sum_j (T - T_{\text{exp}})_j{}^2 \tag{5}$$

Results and Discussion

The root-mean-square deviations (RMSD) between the experimental and calculated values of the measured variables (δP for pressure and δT for temperature) and the optimum binary parameters (a_{ij}) are listed in Table 3.[4−7]

The ternary VLE experimental data are listed in Tables 4 to 6. Table 4 shows the experimental $T - x$ data and Tables 5 and 6 show the experimental $p - x$ data, both together with calculated values of vapor compositions and activity coefficients, predicted by binary parameters. The ternary system is nonideal, showing medium positive deviation from Raoult's law. As seen in Tables 4 to 6, all calculated activity coefficients have values > 1. The deviations between the ternary experimental results and those calculated from the binary temperature-dependent parameters are also presented in these tables. The RMSD in pressure at T = 323.15 K and the RMSD in temperature at P = 66.66 kPa and P = 79.99 kPa are 0.0098, 0.25 K, and 0.38 K, respectively. As can be seen from the data obtained for the ternary system, the UNIQUAC equation gives a good correlation and prediction, simultaneously taking into account all experiments carried out at different pressures and temperatures. These ternary data can be used satisfactorily for the design of the separation process of DMP, acetone, and methanol. These indicate that the UNIQUAC equation can be used for predicting ternary VLE data. It can be used to develop models for correlation and prediction of thermodynamic properties of mixtures.

Conclusions

The ternary isothermal and isobaric VLE data for the ternary system DMP + acetone + methanol at temperature of 323.15 K, and pressures of 66.66 kPa and 79.99 kPa are presented. The ternary system is nonideal, showing medium positive deviation from Raoult's law. The measured ternary results are compared with those calculated from the UNIQUAC equation using temperature-dependent binary parameters, which were obtained from the binary literature data. The results is satisfactory. The ternary VLE data are useful in the design of the more efficient separation process of DMP, acetone, and methanol.

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