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Vapor−Liquid Equilibria of Binary Mixtures Formed by Hexan-1-ol with Chloroethanes and Chloroethenes at 95.6 kPa

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Bubble-point temperatures (at 95.6 kPa) over the entire composition range are measured for the binary mixtures formed by hexan-1-ol with 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, trichloroethene, and tetrachloroehene, employing a Swietoslawski type ebulliometer. Both Wilson and nonrandom two-liquid (NRTL) models are found to represent the measured liquid-phase composition versus bubble-point temperature data well. The computed values of the vapor-phase mole fractions, liquid-phase activity coefficients, and excess Gibbs energies are tabulated and briefly discussed.

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1. Introduction

Hexanol (CAS Registry No. 111-27-3) is the first member of higher alcohol series, in the plasticizers range, which finds extensive application in the manufacturing of plasticizers and lubricants. Hexan-1-ol is also known for its excellent role as a solvent. 1,2-Dichloroethane (CAS Registry No. 107-06-02), a volatile liquid with a pleasant odor, is miscible with other chlorinated solvents. 1,2-Dichloroethane also has high solvency for fats, greases, and waxes. The maximum utility of 1,2-dichloroethane is in the production of vinyl chloride monomer. 1,1,2,2-Tetrachloroethane (CAS Registry No. 79-34-5) is primarily a feed stock for the production of the other important solvents like trichloroethene and tetrachloroethene. 1,1,2-Trichloroethene (CAS Registry No. 79-01-6), a colorless sweet-smelling volatile liquid, is a powerful solvent for a large number of natural as well as synthetic substances. Tetrachloroethene (CAS Registry No. 127-18-4), the most stable of the chloroethanes and chloroethenes, requiring only a small quantity of stabilizer, has no flash point and has excellent solvent properties, which render it useful in the dry cleaning industry as well as in metal cleaning operations. This study leading to the vapor−liquid equilibrium of the binary mixtures formed by hexan-1-ol + chloroethanes and chloroethenes is therefore undertaken in continuation of our recent systematic studies leading to the phase equilibrium of the binary mixtures formed by different types of compounds.[1,2] Dayananda Reddy et al.[3] reported the vapor−liquid equilibria of the hexan-1-ol + 1,2-dichloroethane system at (200 and 700) mmHg. We could not locate any published experimental vapor−liquid equilibrium data on the other systems chosen for the present study. The data presented in this paper are expected to be useful in the design of separation processes (especially by distillation) for mixtures containing the compounds contained in the selected binary mixtures.

2. Experimental Section

2.1. Method. Bubble-point temperatures of gravimetrically prepared liquid mixture samples (over the entire composition range) are measured for the selected systems, making use of a Swietoslawski type ebulliometer, similar to the one described by Hala et al.,[4] and mentioned in some detail in our earlier paper.[1] Experiments are carried out using the method described in our earlier papers.[1,2] On the basis of the comparisons with the available literature on the systems investigated earlier, using the same method and apparatus, and the accuracy of the devices employed by us for these measurements, the measurements reported in this paper are expected to be accurate within ± 0.05 K in temperature, ± 0.05 kPa in pressure, and ± 0.0005 in mole fraction.

2.2. Materials. Purum grade hexan-1-ol (Fluka Chemie AG & Rd H Laborchemikalien, GMBH Co. KG) is dried over molecular sieves and fractionally distilled twice.

Analytical reagent grade 1,2-dichloroethane (BDH Chemicals, Mumbai, India) is further purified by washing with dilute potassium hydroxide solution and water, dried over phosphorus pentoxide, and fractionally distilled twice.

Analytical reagent grade 1,1,2,2-tetrachloroethane (S. D. Fine Chemicals, Boisar, India) is shaken with concentrated sulfuric acid for 10 min at a temperature of $T = 355$ K. Discolored acid is removed, and the acid washing is continued several times until the acid is no longer discolored. The sample is then washed with water, dried over potassium carbonate, and fractionally distilled twice.

Spectroscopic grade trichloroethene (S. D. Fine Chemicals, Boisar, India) is steam-distilled from calcium hydroxide slurry. The organic phase is collected in the temperature range of $T =$ (223 to 243) K, and the ice formed is removed by filtration. The filtrate is subjected to fractional distillation.

Analytical reagent grade tetrachloroethene (S. D. Fine Chemicals, Boisar, India) is dried over anhydrous sodium sulfate and fractionally distilled twice.

The final step of the purification of all of the liquids (fractional distillation) is carried out by means of a packed column of height equivalent to 30 theoretical plates, only a few hours prior to the commencement of the phase equilibrium experiment, and

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Table 1. Comparison of the Density (ρ) and Refractive Index (n_D) with Literature Data[5]

substance	T/K	ρ/kg·m^{-3} this work	ρ/kg·m^{-3} literature	n_D this work	n_D literature
hexan-1-ol	298.15	815.3	815.34	1.4157	1.41570
1,2-dichloroethane	293.15	1252.9	1252.92	1.4196	1.41959
1,1,2,2-tetrachloroethane	293.15	1593.0	1593.02	1.4940	1.49389
trichloroethene	303.15	1451.3	1451.40	1.4750[a]	1.47500[a]
tetrachloroethene	293.15	1623.0	1622.83	1.5058	1.50576

[a] At 297.75 K.

enough care is taken to prevent the absorption of moisture, oxidation, and so forth, during the intervening period. On the basis of the lack of the appearance of multiple significant peaks in the gas chromatograms and the comparison of the physical properties data with the literature values,[5] presented in Table 1, the pure liquids used in the present work are expected to have a mole fraction purity of > 0.999.

Antoine constants collected from the literature[6] are employed in this investigation to compute the saturated vapor pressures of the pure liquids required in obtaining vapor−liquid equilibrium data, as described in the Results and Discussion section. These constants are found to represent the available pure liquid−vapor-pressure data (including the pure liquid boiling temperatures of the present experiments) with an average absolute deviation of 0.5 %.

3. Results and Discussion

The experimental composition (x_1) versus temperature (T) measurements, summarized in Table 2, are fitted to the following models.

The Wilson model expressing the activity coefficients (γ_1 and γ_2) is:

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2[\{\Lambda_{12}/(x_1 + \Lambda_{12}x_2)\} - \{\Lambda_{21}/(x_2 + \Lambda_{21}x_1)\}] \quad (1)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) + x_1[\{\Lambda_{21}/(x_2 + \Lambda_{21}x_1)\} - \{\Lambda_{12}/(x_1 + \Lambda_{12}x_2)\}] \quad (2)$$

where

$$\Lambda_{12} = (V_1^L/V_2^L)\exp[-\{(\lambda_{12} - \lambda_{11})/RT\}] \quad (3)$$

and

$$\Lambda_{21} = (V_2^L/V_1^L)\exp[-\{(\lambda_{12} - \lambda_{22})/RT\}] \quad (4)$$

The nonrandom two-liquid (NRTL) model expressing the activity coefficients is:

$$\ln \gamma_1 = x_{22}[\tau_{21}\{G_{21}/(x_1 + x_2G_{21})\}^2 + \{\tau_{12}G_{12}/(x_2 + G_{12})^2\}] \quad (5)$$

$$\ln \gamma_2 = x_{12}[\tau_{12}\{G_{12}/(x_2 + x_1G_{12})\}^2 + \{\tau_{21}G_{21}/(x_1 + G_{21})^2\}] \quad (6)$$

where

$$\begin{aligned} \ln G_{12} &= -\alpha_{12}\tau_{12} \\ \ln G_{21} &= \alpha_{12}\tau_{21} \\ \tau_{12} &= -g_{12}/RT \end{aligned} \quad (7)$$

$$\begin{aligned} \tau_{21} &= -g_{21}/RT \\ -g_{12} &= g_{12} - g_{22} \\ -g_{21} &= g_{21} - g_{11} \\ \alpha_{12} &= 0.12 \end{aligned} \quad (8)$$

In this case g are the energies of interaction between the species designated by subscripts.

The optimum values of Wilson and NRTL parameters are obtained by minimizing the objective function

$$\varphi = [(P_{cal}/P_{expt}) - 1]^2 \quad (9)$$

where

$$P_{cal} = \gamma_1(\text{Wilson})\, x_1P_1^0 + \gamma_2(\text{Wilson})\, x_2P_2^0 \quad (10)$$

or

$$P_{cal} = \gamma_1(\text{NRTL})\, x_1P_1^0 + \gamma_2(\text{NRTL})\, x_2P_2^0 \quad (11)$$

The Nelder−Mead optimization technique, described by Kuester and Mize,[7] is used. Molar volumes of the pure liquids, obtained from the liquid density data given in Table 1, are used as inputs to the calculation of the Wilson parameters. In the present analysis the vapor phase is assumed to behave as an ideal gas mixture (a reasonable assumption, at pressures close to and below atmospheric pressure), enabling one write and use expressions like

$$y_1P = \gamma_1x_1P_1^0 \quad (12)$$

In view of the polar nature of the common component (hexan-1-ol) as well as the chloroethanes and chloroethenes, it is better to treat the vapor phase as nonideal.

However, we retained the assumption of the behavior of the vapor phase as an ideal gas mixture, as we could not locate satisfactory input data for the application of the models like the Hayden and O'Connell. The results of the representation of the data by the Wilson and NRTL models are summarized in Table 3. Computed values of the vapor-phase mole fractions (y_1), the liquid-phase activity coefficients (γ_1 and γ_2), and the excess Gibbs energy G^E, computed from the optimum parameters of the Wilson and NRTL models, are also given in Table 2.

In an attempt to compare the present data with the available literature data on the 1,2-dichloroethane (1) + hexan-1-ol (2) system, we have plotted the ($t - x$) observations of this work as well as those reported by Dayanda Reddy et al.[3] at 700 mmHg, to find out the agreement between the two sets of data. While the agreement is good at the highest liquid-phase compositions of the more volatile component, it is poor toward lowest liquid-phase compositions.

At the outset, an examination of the values of the data presented in Table 2 indicates that:

(1) The vapor-phase mole fractions of the chloroalkanes for equimolar liquid mixtures of the systems studied are in the order 1,2-dichloroethane (1) + hexan-1-ol (2) > trichloroethylene (1) + hexan-1-ol (2) > tetrachloroethene (1) + hexan-1-ol (2) > 1,1,2,2-tetrachloroethane (1) + hexan-1-ol (2). The order appears to be reverse to that of the normal boiling points, although not in a quantitative way.

(2) The activity coefficients of the chloroalkanes corresponding to equimolar mixtures follow the order 1,2-dichloroethane

Table 2. Measured Liquid-Phase Mole Fraction (x_1) versus Bubble-Point Temperature (T) Data and Computed Values of Vapor-Phase Mole Fractions (y_1), Liquid-Phase Activity Coefficients (γ_1 and γ_2), and Excess Gibbs Energy (G^E)

		Wilson model				NRTL model			
x_1	T/K	y_1	γ_1	γ_2	G^E/J·mol^{-1}	y_1	γ_1	γ_2	G^E/J·mol^{-1}
1,2-Dichloroethane (1) + Hexan-1-ol (2)									
0.0000	428.45	0.0000	1.4457	1.0000	0	0.0000	1.4433	1.0000	0
0.0625	414.55	0.4170	1.3983	1.0015	77.1	0.4167	1.3970	1.0014	76.6
0.1497	400.25	0.6858	1.3316	1.0087	167.2	0.6858	1.3314	1.0086	195.3
0.2122	392.75	0.7817	1.2856	1.0178	219.5	0.7818	1.2858	1.0178	219.6
0.2604	388.05	0.8295	1.2520	1.0273	253.1	0.8296	1.2523	1.0273	253.3
0.3229	383.05	0.8722	1.2112	1.0430	287.5	0.8722	1.2115	1.0430	287.8
0.4132	377.15	0.9120	1.1585	1.0727	319.8	0.9120	1.1587	1.0729	320.3
0.4757	373.85	0.9308	1.1266	1.0987	329.7	0.9307	1.1266	1.0991	330.3
0.5137	371.95	0.9400	1.1089	1.1169	330.5	0.9400	1.1089	1.1174	331.2
0.5762	369.25	0.9526	1.0829	1.1511	324.0	0.9525	1.0827	1.1518	324.4
0.6138	367.75	0.9590	1.0689	1.1744	314.9	0.9589	1.0687	1.1753	315.4
0.6763	365.45	0.9681	1.0486	1.2181	291.6	0.9681	1.0483	1.2193	292.0
0.7406	363.15	0.9761	1.0314	1.2704	256.6	0.9761	1.0311	1.2717	256.7
0.8031	361.15	0.9828	1.0182	1.3293	211.8	0.9828	1.0180	1.3306	211.9
0.8656	359.25	0.9888	1.0086	1.3974	156.5	0.9888	1.0084	1.3983	156.1
0.9345	357.15	0.9948	1.0021	1.4848	82.7	0.9948	1.0020	1.4847	82.4
1.0000	355.15	1.0000	1.0000	1.5821	0	1.0000	1.0000	1.5800	0
1,1,2,2-Tetrachloroethane (1) + Hexan-1-ol (2)									
0.0000	428.45	0.0000	2.7854	1.0000	0	0.0000	2.3243	1.0000	0
0.0625	425.15	0.1497	1.9440	1.0109	182.8	0.1461	1.8856	1.0066	162.0
0.1164	423.95	0.2212	1.5999	1.0301	285.2	0.2259	1.6305	1.0210	265.4
0.1792	422.65	0.2848	1.3767	1.0570	361.2	0.2944	1.4253	1.0449	350.0
0.2832	421.35	0.3756	1.1880	1.1037	418.7	0.3837	1.2180	1.0944	421.2
0.3457	420.75	0.4279	1.1262	1.1309	425.3	0.4325	1.1423	1.1268	434.1
0.4082	420.25	0.4801	1.0848	1.1566	417.0	0.4810	1.0899	1.1589	414.7
0.5131	419.65	0.5688	1.0425	1.1958	378.5	0.5650	1.0367	1.2083	386.0
0.5756	419.15	0.6226	1.0274	1.2166	344.2	0.6175	1.0190	1.2330	347.5
0.6381	418.85	0.6770	1.0170	1.2356	304.1	0.6719	1.0081	1.2531	302.3
0.7006	418.55	0.7320	1.0100	1.2528	259.1	0.7280	1.0021	1.2678	252.1
0.7631	418.25	0.7875	1.0054	1.2682	210.0	0.7853	0.9994	1.2766	199.4
0.8256	417.95	0.8434	1.0025	1.2820	157.7	0.8430	0.9988	1.2792	145.8
0.8881	417.65	0.8995	1.0009	1.2942	103.0	0.9005	0.9992	1.2755	92.1
0.9131	417.55	0.9119	1.0005	1.2987	80.1	0.9233	0.9994	1.2723	70.7
1.0000	417.25	1.0000	1.0000	1.3125	0	1.0000	1.0000	1.2532	0
Trichloroethene (1) + Hexan-1-ol (2)									
0.0000	428.45	0.0000	1.0662	1.0000	0	0.0000	1.0585	1.0000	0
0.0625	419.35	0.3099	1.0471	1.0005	11.68	0.3091	1.0438	1.0004	10.65
0.1343	410.25	0.5371	1.0305	1.0020	19.66	0.5371	1.0301	1.0015	18.01
0.1968	403.55	0.6662	1.0199	1.0038	23.24	0.6666	1.0207	1.0030	21.60
0.2368	399.95	0.7270	1.0146	1.0049	23.82	0.7274	1.0157	1.0040	23.40
0.2993	393.95	0.7984	1.0084	1.0067	23.53	0.7988	1.0095	1.0056	22.09
0.3829	387.45	0.8636	1.0031	1.0086	20.84	0.8639	1.0037	1.0076	19.61
0.4454	383.25	0.8977	1.0007	1.0096	17.88	0.8978	1.0009	1.0087	16.59
0.5206	378.65	0.9276	0.9991	1.0102	13.84	0.9276	0.9989	1.0094	13.37
0.5831	375.25	0.9460	0.9986	1.0100	10.40	0.9460	0.9981	1.0094	8.71
0.6768	370.65	0.9662	0.9989	1.0086	6.91	0.9962	0.9980	1.0079	3.66
0.7393	367.85	0.9761	0.9993	1.0070	3.98	0.9761	0.9983	1.0058	0.76
0.8072	365.15	0.9846	0.9996	1.0046	1.71	0.9846	0.9989	1.0025	−1.23
0.8697	362.75	0.9907	0.9996	1.0019	−0.30	0.9907	0.9994	0.9984	−2.20
0.9262	360.85	0.9952	0.9999	0.9990	−2.80	0.9953	0.9998	0.9938	−1.93
1.0000	358.45	1.0000	1.0000	0.9946	0	1.0000	1.0000	0.9866	0
Tetrachloroethene (1) + Hexan-1-ol (2)									
0.0000	428.45	0.0000	1.9934	1.0000	0	0.0000	1.9579	1.0000	0
0.0625	422.05	0.2404	1.7724	1.0041	139.0	0.2392	1.7609	1.0036	136.0
0.1198	417.75	0.3782	1.6126	1.0141	241.7	0.3783	1.6122	1.0130	238.2
0.1823	414.25	0.4821	1.4752	1.0310	330.1	0.4834	1.4799	1.0291	326.9
0.2900	409.65	0.6039	1.3044	1.0722	431.2	0.6055	1.3095	1.0697	429.3
0.3525	407.45	0.6567	1.2382	1.1020	468.2	0.6580	1.2365	1.0998	462.2
0.4051	405.85	0.6953	1.1842	1.1302	464.7	0.6962	1.1864	1.1284	502.1
0.4676	404.85	0.7364	1.1373	1.1670	479.3	0.7367	1.1381	1.1659	478.7
0.5214	402.75	0.7687	1.1048	1.2013	467.9	0.7686	1.1045	1.2011	466.1
0.5839	401.15	0.8036	1.0744	1.2443	443.1	0.8033	1.0734	1.2448	441.9
0.6476	399.65	0.8370	1.0504	1.2913	405.2	0.8367	1.0490	1.2922	403.1
0.7101	398.25	0.8683	1.0323	1.3405	356.0	0.8680	1.0309	1.3411	351.2
0.7861	396.65	0.9046	1.0166	1.4044	282.2	0.9046	1.0155	1.4031	278.8
0.8351	395.55	0.9273	1.0095	1.4478	226.7	0.9274	1.0087	1.4442	222.3
0.9168	393.85	0.9639	1.0023	1.5243	121.8	0.9641	1.0020	1.5141	118.9
1.0000	392.15	1.0000	1.0000	1.6072	0	1.0000	1.0000	1.5859	0

Table 3. Model Parameters (Units: K)[a]

	Wilson model			NRTL model			
system	$(\lambda_{12} - \lambda_{11})/R$	$(\lambda_{12} - \lambda_{22})/R$	σ	α	$(g_{12} - g_{22})/R$	$(g_{21} - g_{11})/R$	σ
1,2-dichloroethane (1) + hexan-1-ol (2)	677.50	101.27	0.03	0.12	140.47	22.17	0.03
1,1,2,2-tetrachloroethane (1) + hexan-1-ol (2)	751.93	−234.97	0.06	0.12	−86.88	1469.59	0.12
trichloroethene (1) + hexan-1-ol (2)	266.66	−190.05	0.04	0.12	−465.70	549.48	0.04
tetrachloroethene (1) + hexan-1-ol (2)	338.05	−404.75	0.03	0.12	−462.99	769.12	0.06

[a] $\sigma = \sum[(T_{\text{expt}} - T_{\text{cal}})^2/N]^{0.5}$.

(1) + hexan-1-ol (2) > tetrachloroethene (2) > 1,1,2,2-tetrachloroethane (1) + hexan-1-ol (2) > trichloroethene (1) + hexan-1-ol (2).

(3) The activity coefficients of hexan-1-ol (the common component) corresponding to equimolar mixtures are in the order 1,1,2,2-tetrachloroethane (1) + hexan-1-ol (2) > tetrachloroethene (1) + hexan-1-ol (2) > 1,2-dichloroethane (1) + hexan-1-ol (2) > trichloroethene (1) + hexan-1-ol (2).

(4) The activity coefficients of both of the components in the case of 1,2-dichloroethane (1) + hexan-1-ol (2), 1,1,2,2-tetrachloroethane (1) + hexan-1-ol (2), and tetrachloroethene (1) + hexan-1-ol (2) are throughout greater than one indicating positive deviations from the Raoult's law, over the whole composition range.

(5) Rather insignificant negative deviations from Raoult's law are noticed for the 1,1,2-trichloroethene (1) + hexan-1-ol (2) system beyond a liquid phase mole fraction greater than 0.5 for the more volatile component.

(6) The excess Gibbs energies for equimolar mixtures are in the order tetrachloroetene (1) + hexan-1-ol (2) > 1,1,2,2-tetrachloroethane (1) + hexan-1-ol (2) > 1,2-dichloroethane (1) + hexan-1-ol (2) > trichloroethene (1) + hexan-1-ol (2). However, it is interesting to note that the excess Gibbs energies for trichloroethane (1) + 1-hexanol (2) are much smaller than those for the other systems over the entire composition range.

4. Conclusion

Experimental work leading to the vapor−liquid equilibria of the binary mixtures formed by hexan-1-ol with two chloroethanes (1,2-dichloroethane and 1,1,2,2-tetrachloroethane) and two chloroethenes (trichloroethene and tetrachloroethene) has been carried out. The results have been presented and discussed in the previous section. It is of interest to note that all of the four systems investigated do not form azeotropes under the conditions studied. In view of the care taken during the experimentation and satisfactory representation of the measurements by both Wilson and NRTL models, the information presented in the paper is expected to be useful for engineering design work.

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