Figure 2. Vapor compositions and excess Gibbs free energies for the system isobutyl methyl ketone (1)-1-hexanol (2) at 200 and 700 mmHg.

The vapor composition (Y), activity coefficients, and excess Gibbs free energies are presented in Tables VII–X and represented in Figures 1 and 2. The excess Gibbs free energies are positive over the entire range of composition. The G^E values for the two binary systems fall in the order 1-pentanol, 1-hexanol. The positive G^E values over the entire range of composition indicated that there is a strong attraction between unlike molecules through hydrogen bonding.

Glossary

A, B, C	Antoine constants
P	pressure, mmHg
t	temperature, °C
x	mole fraction in liquid phase
y	vapor composition

Greek Letters

γ	activity coefficient
Λ	Wilson parameter

Subscripts

1	isobutyl methyl ketone
2	normal alcohols

Registry No. Isobutyl methyl ketone, 108-10-1; 1-pentanol, 71-41-0; 1-hexanol, 111-27-3.

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Activity Coefficients and Excess Gibbs Free Energies of 1,2-Dichloroethane with 1-Pentanol and 1-Hexanol

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Vapor–liquid equilibrium data for the systems 1,2-dichloroethane (1)-1-pentanol (2) and 1,2-dichloroethane–1-hexanol (2) were measured by the indirect method from the composition vs. boiling point (x–t) measurements made in a standard Swietoslawski type ebulliometer. The measurements were made at 200 and 700 mmHg. The experimental t–x data were used to estimate Wilson parameters; these in turn are useful to calculate vapor compositions, boiling points, and activity coefficients. These activity coefficients are useful to calculate excess Gibbs free energy G^E.

Introduction

Evaporation has been used as an effective means of separation in chemical processing. Evidently an accurate and complete knowledge of vapor–liquid equilibrium on the mixture under consideration is necessary for the design of distillation equipment. Generally vapor–liquid equilibrium data are obtainable under two fixed conditions, namely, isothermal and isobaric. Most distillation processes are carried out at constant pressure rather than constant temperature. Temperature–composition curves are more practical in making engineering calculations such as the number of plates, although for theoretical consideration the pressure–composition curves are preferable. As part of a continuing study of alcohol–chloroethane systems, vapor–liquid equilibrium data on 1,2-dichloroethane–1-pentanol and 1,2-dichloroethane–1-hexanol systems are determined at 200 and 700 mmHg, because the data on these systems have not been reported in literature.

Experimental Section

The vapor–liquid equilibrium measurements were studied in a standard Swietoslawski type ebulliometer (1). The ebulliom-

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Table I. Antoine Constants and the Standard Deviation for the Pure Compounds

compound	A	B	C	σ_P, %
1,2-dichloroethane	6.66301	1073.99	200.4	0.30
1-pentanol	7.7351	1644.58	201.3	0.41
1-hexanol	7.8066	1729.49	194.1	0.60

eter was connected to a vacuum system. Pressure were measured with a mercury manometer with an accuracy of ±1 mmHg. The temperatures were measured with a PT100 thermometer which gave an accuracy of ±0.1 °C. The detailed procedure was described previously (*1*).

Isobaric Binary Systems. The isobaric boiling points of the systems 1,2-dichloroethane (1)-1-pentanol (2) and 1,2-dichloroethane (1)-1-hexanol (2) were determined over the entire range of composition. Mixtures of different compositions were prepared by mixing known weights of the pure materials. The boiling points for the known binary compositions were measured at 200 and 700 mmHg. The boiling point of a specified composition was first measured at 200 mmHg. Then the pressure was raised to 700 mmHg and the boiling point was determined. The system was brought back to 200 mmHg where the boiling point measurement was repeated, and finally the measurement was repeated at 700 mmHg, thereby obtaining duplicate sets at both the pressures. The procedure also helps us detect any possible dissociation and loss of material in the mixture under study.

Purification of Materials. 1,2-Dichloroethane (BDH) was further purified by the standard methods described by Riddick and Bunger. 1-Pentanol (E. Merck) and 1-hexanol (BDH) were dried over Drierite and fractionally distilled. The purity of the samples was checked by measuring densities, boiling points, and refractive indices. The densities were measured with a bicapillary pycnometer which gave an accuracy of 5 parts in 10^5. Refractive indices were determined by using Abbe's refractometer which gave an accuracy of ±0.0002. The boiling points were determined with a Swietoslawski ebulliometer which gave an accuracy of ±0.2 °C. The measured values are in good agreement with the literature values (*2*, *3*).

Results and Discussion

Isobaric *t–x* measurements are used for the data reduction. The model for expressing the composition and temperature dependence is chosen to be the Wilson equation (*4*)

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

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

The Wilson Parameters Λ_{12} and Λ_{21} are given by

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

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

where V_1^L and V_2^L are liquid molar volumes $(\lambda_{12} - \lambda_{11})$ and $(\lambda_{12} - \lambda_{22})$ are temperature-independent (to some extent) Wilson parameters λ's are the energies of interaction between the molecules designated in the subscripts. The optimum Wilson parameters λ_{12} and λ_{21} are obtained by minimizing the objective

Table II. Wilson Parameters with Standard Deviation

system	P, mmHg	$(\lambda_{12} - \lambda_{11})/R$, K	$(\lambda_{12} - \lambda_{22})/R$, K	σ_t, °C
1,2-dichloroethane (1) 1-pentanol (2)	200	59.3120	454.410	0.50
1,2-dichloroethane (1) 1-pentanol (2)	700	58.0421	362.901	0.13
1,2-dichloroethane (1) 1-hexanol (2)	200	762.350	−37.5518	0.48
1,2-dichloroethane (1) 1-hexanol (2)	700	1044.10	−154.000	0.48

Table III. 1,2-Dichloroethane (1)-1-Pentanol (2) *t–x* Data at 200 mmHg

x	t(exptl), °C	t(calcd),[a] °C	t(ideal), °C	t(exptl) − t(calcd), °C
0.1538	74.9	74.1	84.3	0.8
0.1538	75.0	74.1	84.3	0.9
0.2892	62.1	62.8	73.5	−0.7
0.2892	62.1	62.8	73.5	−0.7
0.3600	59.0	59.1	69.1	−0.1
0.3600	59.0	59.1	69.1	−0.1
0.4932	53.9	54.2	62.1	−0.3
0.4932	53.9	54.2	62.1	−0.3
0.5068	53.6	53.8	61.5	−0.2
0.5068	53.6	53.8	61.5	−0.2
0.6963	50.0	49.9	54.2	0.1
0.6963	50.0	49.9	54.2	0.1
0.7687	49.2	48.9	51.9	0.3
0.7687	49.1	48.9	51.9	0.2
0.8303	48.4	48.1	50.1	0.3
0.8303	48.5	48.1	50.1	0.4
0.9570	47.1	46.5	46.8	0.6
0.9570	47.1	46.5	46.8	0.6

[a] Using Wilson's equation.

Table IV. 1,2-Dichloroethane (1)-1-Pentanol (2) *t–x* Data at 700 mmHg

x	t(exptl), °C	t(calcd),[a] °C	t(ideal), °C	t(exptl) − t(calcd), °C
0.1538[b]	115.0	113.5	121.7	1.5
0.1538[b]	115.0	113.5	121.7	1.5
0.2892	102.0	102.2	111.8	−0.2
0.2892	102.0	102.2	111.8	−0.2
0.3600	98.0	98.0	107.4	0.0
0.3600	98.0	98.0	107.4	0.0
0.4932	92.3	92.2	100.0	0.1
0.4932	92.4	92.2	100.0	0.2
0.5068	91.8	91.7	99.3	0.1
0.5068	91.9	91.7	99.3	0.2
0.6963	86.5	86.6	91.0	−0.1
0.6963	86.5	86.6	91.0	−0.1
0.7687	85.0	85.1	88.3	−0.1
0.7687	85.1	85.1	88.3	0.0
0.8303	83.8	84.0	86.1	−0.2
0.8303	83.9	84.0	86.1	−0.1
0.9570	81.7	81.7	82.1	+0.0
0.9570	81.8	81.7	82.1	0.1

[a] Using Wilson's equation. [b] Points rejected from analysis.

function ϕ, using Nelder–Mead optimization techniques (*5*), and the values are presented in Table I along with the standard deviation of the fit.

$$\phi = \sum(P_{\text{calcd}}/P_{\text{exptl}} - 1.0)^2 \quad (5)$$

Since the prediction of vapor–liquid equilibrium data involves the vapor pressure data of the pure compounds the same has been determined for 1,2-dichloroethane, 1-pentanol, and 1-hexanol. The Antoine constants for the pure compounds were obtained by nonlinear regression analysis of the experimental data. The obtained Antoine constants are presented in Table II with the standard deviation. The measured boiling points, calculated boiling points using Wilson equation, and ideal boiling points are

Table V. 1,2-Dichloroethane (1)-1-Hexanol (2) t-x Data at 200 mmHg

x	t(exptl), °C	t(calcd),[a] °C	t(exptl) − t(calcd), °C
0.1638	64.4	64.7	−0.3
0.1638	64.5	64.7	−0.2
0.2731	61.2	60.6	0.6
0.2731	61.3	60.6	0.7
0.3889	58.0	58.0	0.0
0.3889	58.0	58.0	0.0
0.4504	56.5	56.8	−0.3
0.4504	56.6	56.8	−0.2
0.5336	54.8	55.3	−0.5
0.5336	54.9	55.3	−0.4
0.6168	52.2	53.7	−1.5
0.6168	52.3	53.7	−1.4
0.7551	51.0	51.0	0.0
0.7551	51.0	51.0	0.0
0.8688	49.2	48.7	0.5
0.8688	49.3	48.7	0.6
0.9357	48.0	47.3	0.7
0.9357	48.1	47.3	0.8

[a] Using Wilson's equation.

Table VI. 1,2-Dichloroethane (1)-1-Hexanol (2) t-x Data at 700 mmHg

x	t(exptl), °C	t(calcd),[a] °C	t(exptl) − t(calcd), °C
0.1638	106.0	106.1	−0.1
0.1638	105.9	106.1	−0.2
0.2731	102.2	101.8	0.4
0.2731	102.4	101.8	0.6
0.3889	98.2	98.2	0.0
0.3889	98.3	98.2	0.1
0.4504	96.3	96.4	−0.1
0.4504	96.4	96.4	0.0
0.5336	93.8	94.1	−0.3
0.5336	93.8	94.1	−0.3
0.6168[b]	90.2	91.7	−1.5
0.6168[b]	90.2	91.7	−1.5
0.7551	87.2	87.8	−0.6
0.7551	87.3	87.8	−0.5
0.8688	83.8	84.6	−0.8
0.8688	84.0	84.6	−0.6
0.9357	82.0	82.7	−0.7
0.9357	82.1	82.1	−0.6

[a] Using Wilson's equation. [b] Points rejected from analysis.

presented in Tables III–VI. If vapor-phase nonidealities are neglected, which is justified at these low pressures, the vapor compositions can be calculated by using the following equation

$$y_1 = \frac{x_1 P_1{}^S \gamma_1{}^S}{P_{calcd}} \quad (6)$$

The excess Gibbs free energies were calculated by using activity coefficients

$$G^E/RT = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \quad (7)$$

The vapor compositions, activity coefficients, and excess Gibbs free energies are presented in Tables VII–X.

The excess Gibbs free energies are positive over the entire range of composition. The excess Gibbs free energies are increasing from 1-pentanol to 1-hexanol. From the vapor composition vs. mole fraction data, we can say that the systems are nonideal.

Glossary

A, B, C	Antoine constants
P	pressure, mmHg
t	temperature, °C

Table VII. Vapor Compositions, Activity Coefficients, and Excess Free Energies for the System 1,2-Dichloroethane (1)-1-Pentanol (2) at 200 mmHg

x	y(calcd)	t(calcd), °C	γ_1	γ_2	G^E, J mol^{-1}
0.00	0.0000	101.3	1.8769	1.0000	
0.05	0.4211	89.8	1.8374	1.009	91
0.10	0.6313	81.1	1.7914	1.0038	175
0.15	0.7458	74.5	1.7409	1.0090	253
0.20	0.8137	69.5	1.6878	1.0169	324
0.25	0.8570	65.4	1.6333	1.0279	388
0.30	0.8863	62.2	1.5784	1.0428	446
0.35	0.9070	59.6	1.5236	1.0621	497
0.40	0.9223	57.4	1.4695	1.0870	540
0.45	0.9339	55.5	1.4164	1.1185	574
0.50	0.9431	54.0	1.3645	1.1586	599
0.55	0.9504	52.7	1.3141	1.2094	615
0.60	0.9565	51.6	1.2655	1.2745	619
0.65	0.9617	50.7	1.2189	1.3586	611
0.70	0.9662	49.8	1.1746	1.4694	589
0.75	0.9703	49.1	1.220	1.6188	552
0.80	0.9742	48.5	1.0945	1.8268	496
0.85	0.9783	47.8	1.0600	2.1298	418
0.90	0.9829	47.2	1.0307	2.5997	315
0.95	0.9893	46.6	1.0091	3.3985	179
1.00	1.0000	45.8	1.0000		

Table VIII. Vapor Compositions, Activity Coefficients, and Excess Gibbs Free Energies for the System 1,2-Dichloroethane (1)-1-Pentanol (2) at 700 mmHg

x	y(calcd)	t(calcd), °C	γ_1	γ_2	G^E, J mol^{-1}
0.00	0.0000	135.0	1.7013	1.0000	
0.05	0.2850	126.7	1.6634	1.0008	84
0.10	0.4716	119.7	1.6232	1.0033	162
0.15	0.5971	113.9	1.5811	1.0079	234
0.20	0.6839	109.0	1.5379	1.0149	299
0.25	0.7459	104.9	1.4940	1.0247	359
0.30	0.7915	101.5	1.4499	1.0377	412
0.35	0.8260	98.5	1.4060	1.0545	457
0.40	0.8528	96.0	1.3626	1.0760	495
0.45	0.8740	93.8	1.3200	1.1032	525
0.50	0.8912	92.0	1.2785	1.1372	547
0.55	0.9055	90.3	1.2383	1.1798	558
0.60	0.9176	88.9	1.1996	1.2334	559
0.65	0.9282	87.6	1.1628	1.3012	549
0.70	0.9376	86.5	1.1280	1.3880	526
0.75	0.9464	85.5	1.0958	1.5008	488
0.80	0.9548	84.5	1.0666	1.6503	434
0.85	0.9635	83.6	1.0411	1.8541	362
0.90	0.9730	82.8	1.0203	2.1420	268
0.95	0.9845	81.9	1.0057	2.5691	149
1.00	1.0000				

Table IX. Vapor Compositions, Activity Coefficients, and Excess Free Energies for the System 1,2-Dichloroethane(1)-1-Hexanol (2) at 200 mmHg

x	y(calcd)	t(calcd), °C	γ_1	γ_2	G^E, J mol^{-1}
0.00	0.0000	120.0	5.9821	1.0000	
0.05	0.8467	80.3	4.9287	1.0099	227
0.10	0.9161	69.9	3.7464	1.0359	450
0.15	0.9364	65.5	2.9698	1.0729	604
0.20	0.9462	63.0	2.4573	1.1183	724
0.25	0.9524	61.3	2.1032	1.1711	814
0.30	0.9569	60.0	1.8478	1.2311	879
0.35	0.9607	58.8	1.6573	1.2983	920
0.40	0.9640	57.8	1.5114	1.3731	941
0.45	0.9671	56.8	1.3973	1.4562	943
0.50	0.9700	55.9	1.3068	1.5482	928
0.55	0.9729	55.0	1.2343	1.6502	896
0.60	0.9758	54.0	1.1759	1.7633	848
0.65	0.9786	53.1	1.1289	1.8889	787
0.70	0.8915	52.1	1.0911	2.0287	711
0.75	0.9845	51.1	1.0613	2.1844	623
0.80	0.9875	50.1	1.0381	2.3585	521
0.85	0.9905	49.1	1.0210	2.5536	408
0.90	0.9936	48.0	1.0091	2.7728	283
0.95	0.9968	46.9	1.0023	3.0198	147
1.00	1.0000	45.8	1.0000	3.2992	

Table X. Vapor Compositions, Activity Coefficients, and
Excess Gibbs Free Energies for the System
1,2-Dichloroethane (1)-1-Hexanol (2) at 700 mmHg

x	y(calcd)	t(calcd), °C	γ_1	γ_2	G^E, J mol^{-1}
0.00	0.0000	154.5	7.9930	1.0000	
0.05	0.7370	118.9	5.1818	1.0148	302
0.10	0.8183	110.5	3.5405	1.0481	518
0.15	0.8479	106.8	2.6905	1.0909	676
0.20	0.8654	104.5	2.1931	1.1398	791
0.25	0.8785	102.6	1.8732	1.1937	871
0.30	0.8897	100.9	1.6534	1.2520	922
0.35	0.8999	99.4	1.4952	1.3146	950
0.40	0.9093	97.9	1.3774	1.3813	956
0.45	0.9184	96.4	1.2877	1.4521	943
0.50	0.9271	95.0	1.2180	1.5273	914
0.55	0.9355	93.6	1.1635	1.6068	871
0.60	0.9436	92.2	1.1205	1.6909	814
0.65	0.9516	90.8	1.0866	1.7796	745
0.70	0.9592	89.4	1.0601	1.8732	665
0.75	0.9667	87.9	1.0396	1.9718	574
0.80	0.9739	86.5	1.0241	2.0756	475
0.85	0.9808	85.1	1.0130	2.1847	367
0.90	0.9875	83.7	1.0055	2.2993	252
0.95	0.9939	82.3	1.0013	2.4197	129
1.00	1.0000	80.9	1.0000	2.5460	

x	mole fraction in liquid phase
y	vapor composition
T	critical temperature
U	molar volume

Greek Letters

γ	activity coefficient
Λ	Wilson parameters

Subscripts

1	1,2-dichloroethane
2	normal alcohols

Registry No. 1,2-Dichloroethane, 107-06-2; 1-pentanol, 71-41-0; 1-hexanol, 111-27-3.

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Solubility of CO in Aqueous Mixtures of Methanol, Acetic Acid, Ethanol, and Propionic Acid[†]

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The solubility of carbon monoxide (CO) in water–methanol, water–acetic acid, water–ethanol, and water–propionic acid has been determined in a temperature range of 298–448 K and a pressure range of 1×10^3–8×10^3 kPa. The values of the enthalpy change of solution and Henry's coefficients have been determined and the solubility data correlated by using the equation in $H = k_1 + k_2/T + k_3(X)(1/298 - 1/T) + k_4 \ln(1 + X)$. For each system, the values of the constants have been evaluated. The results predicted with this correlation agreed well with the experimental data within 3–4% error.

Introduction

Solubility data for gases in liquids is most essential in studies on gas–liquid and gas–liquid–solid reactions. Several industrial processes involve gas–liquid reactions wherein the liquid-phase composition changes during the course of a reaction. In such cases, determination of solubility of gaseous reactants in liquid mixtures of different compositions becomes essential. The objective of this work was to determine solubility of carbon

monoxide (CO) in various liquid mixtures involved in industrial carbonylation processes such as carbonylation of methanol to acetic acid (1) and ethanol to propionic acid (2). The earlier studies on CO solubility (3, 4) are mainly on binary systems at atmospheric pressure and in a lower temperature range. However, there are no published data available for liquid mixtures encountered in the above processes at higher temperatures and pressures. Therefore, in this work solubility of CO was determined at different temperatures and pressures in liquid mixtures under conditions of practical interest in carbonylation processes. It was also the objective of this work to develop a suitable correlation based on the experimental data.

Experimental Section

The solubility data were obtained by using a technique described by Radhakrishnan et al. (5) in which desorbed gas from a saturated sample was measured by using a specially designed apparatus. The details of the apparatus and procedure are described by Radhakrishnan et al. (5). Carbon monoxide gas generated in our own laboratory by dehydration of formic acid, and with a purity greater than 99.5%, was used. The solvents used in this work were supplied by BDH Laboratories and freshly distilled before use. The purity of the solvents as evaluated by

[†] NCL Communication No. 3522.