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Isothermal Vapor−Liquid Equilibria of Ethyl Acetate + Dibromomethane or + Bromochloromethane or + 1,2-Dichloroethane or +1-Bromo-2-chloroethane at T = 313.15 K

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Isothermal vapor−liquid equilibria (VLE) at 313.15 K have been measured for liquid ethyl acetate + dibromomethane or + bromochloromethane or + 1,2-dichloroethane or + 1-bromo-2-chloroethane mixtures. The VLE data were reduced using the Redlich−Kister equation by taking into consideration the vapor-phase nonideality in terms of the second molar virial coefficients, and the liquid activity coefficients were correlated by means of the Margules, van Laar, Wilson, NRTL, and UNIQUAC equations. The thermodynamic consistency of the experimental data was checked by means of the test of Van Ness et al. in the version of Fredenslund et al. The excess molar Gibbs energies of all of the studied mixtures are negative and range from −75 J mol^{-1} for ethyl acetate + 1-bromo-2-chloroethane to −300 J mol^{-1} for ethyl acetate + bromochloromethane at a mole fraction of x = 0.5.

Introduction

The thermodynamic behavior of mixtures containing haloalkanes is of considerable interest because of their theoretical and industrial importance. Following our systematic study of the thermodynamics of binary mixtures containing mono- and polyhaloalkanes,[1] we report in this paper the isothermal vapor−liquid equilibrium, VLE, at 313.15 K for ethyl acetate + dibromomethane or + bromochloromethane or + 1,2-dichloroethane or +1-bromo-2-chloroethane. As far as we know, there are no previous measurements on these mixtures.

Experimental Section

Materials. Ethyl acetate (purity >99.5 mol %), dibromomethane (purity >98.5 mol %), and 1,2-dichloroethane (purity >99.5 mol %) were obtained from Fluka AG Buchs; bromochloromethane (purity >99.0 mol %) and 1-bromo-2-chloroethane (purity >98.0 mol %) were obtained from Aldrich Chemical Co. All of the liquids were used without further purification.

In Table 1, we compare the measured densities and vapor pressures of the products with literature values.

Apparatus and Procedure. Vapor−liquid equilibrium data were taken at constant temperature in a dynamic still designed by Berro et al.[2] The temperature T inside the equilibrium cell was measured with a precision of 0.01 K by means of a Digitec digital thermometer (Digitec Corp., model 5831). The pressure P was measured by means of a digiquartz transmitter (Paroscientific Inc., model 1015A), calibrated in the pressure range of 0−0.1 MPa. The accuracy of the pressure measurements is 0.01%. Liquid and vapor mole fractions x_1 and y_1, respectively, were determined by densimetric analysis using an Anton Paar model DMA 60 densimeter equipped with a DMA 602 cell in a flow system as described in Muñoz Embid et al.[1] The densimeter calibration was performed at atmospheric pressure by using doubly distilled and degassed water, carbontetrachloride, and cyclohexane. The vibrating-tube temperature was measured by means of an Anton Paar DM 100-30 digital thermometer and was regulated to better than 0.01 K using a Neslab RTE-210 thermostat. The uncertainty of the composition measurements was estimated to be ±0.0001 mole fraction. Molar excess volumes have been determined from density measurements, carried out with the same densimeter.

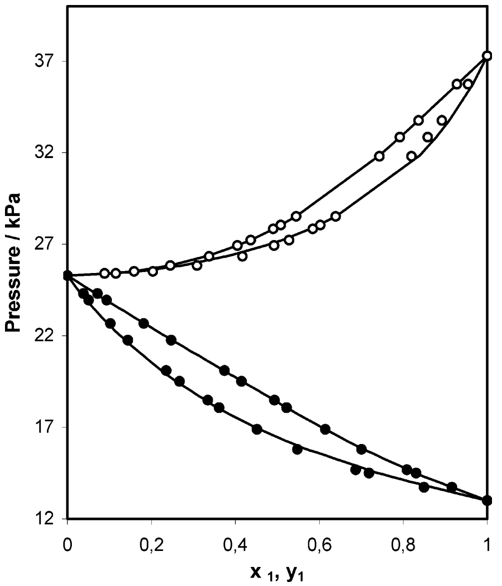

Figure 1. Vapor−liquid equilibrium diagrams at 313.15 K. Pressure, P, as a function of mole fraction in the liquid, x_1, or vapor, y_1, phase. Continuous curve and smoothed values, eq 1; points, direct experimental values: ●, dibromomethane (1) + ethyl acetate (2); ○, bromochloromethane (1) + ethyl acetate (2).

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Table 1. Densities ρ_i^0, Vapor Pressure P_i^0, Molar Second Virial Coefficients B_{ii}, and Liquid Molar Volume V_i^0 of Pure Components

	ρ_i^0 (298.15 K)/ g cm^{-3}		P_i^0 (313.15 K)/ kPa		B_{ii}(313.15 K)/ cm^3 mol^{-1}	V_i^0 (313.15 K)/ cm^3 mol^{-1}
	this work	lit	this work	lit[8]	this work[3,4]	this work
ethyl acetate	0.89497	0.89400[8]	25.296	25.040	−1891	101
dibromo-methane	2.47837	2.48420[8]	13.012	12.430	−845	71
bromochloro-methane	1.92488	1.92300[8]	37.285	37.190	−683	69
1,2-dichloro-ethane	1.24659	1.24637[9]	21.047	20.720	−1006	81
1-bromo-2-chloroethane	1.72788	1.73015[9]	8.910	8.770	−1014	84

Table 2. Experimental Vapor−Liquid Equilibrium Pressure P at 313.15 K as a Function of Liquid Mole Fraction x_1 and Vapor Mole Fraction y_1

x_1	y_1	P/kPa	γ_1	γ_2	G^E/RT	x_1	y_1	P/kPa	γ_1	γ_2	G^E/RT
					Dibromomethane (1) + Ethyl Acetate (2)						
0.0710	0.0315	24.306	1.0003	0.8556	−0.0088	0.5222	0.3701	18.088	0.9453	0.9734	−0.0431
0.0936	0.0429	23.948	0.9987	0.8728	−0.0128	0.6137	0.4568	16.902	0.9322	0.9822	−0.0429
0.1817	0.0882	22.685	0.9950	0.8778	−0.0226	0.6855	0.5355	16.055	0.9283	0.9866	−0.0384
0.2469	0.1365	21.755	0.9791	0.9133	−0.0297	0.7001	0.5610	15.808	0.9143	0.9900	−0.0419
0.3738	0.2339	20.094	1.0192	0.9226	−0.0362	0.8084	0.6908	14.694	0.9082	0.9938	−0.0290
0.4147	0.2669	19.520	0.9667	0.9445	−0.0397	0.8306	0.7166	14.510	0.8880	0.9981	−0.0241
0.4929	0.3405	18.496	0.9494	0.9671	−0.0415	0.9154	0.8192	13.733	0.8803	1.0003	−0.0129
					Bromochloromethane (1) + Ethyl Acetate (2)						
0.0887	0.0898	25.402	0.9983	0.6663	−0.0305	0.5083	0.6072	28.049	0.8559	0.9309	−0.1113
0.1583	0.1661	25.515	0.9867	0.7237	−0.0537	0.5445	0.6460	28.533	0.8429	0.9431	−0.1112
0.2451	0.2686	25.851	0.9782	0.7515	−0.0759	0.7428	0.8413	31.797	0.8125	0.9615	−0.0908
0.3372	0.3789	26.348	0.9646	0.7793	−0.0961	0.7916	0.8801	32.844	0.7747	0.9825	−0.0769
0.4046	0.4535	26.935	0.9010	0.8875	−0.1041	0.8362	0.9116	33.768	0.7399	0.9929	−0.0642
0.4370	0.4973	27.219	0.8863	0.9034	−0.1083	0.9274	0.9644	35.746	0.7164	0.9990	−0.0310
0.4901	0.5788	27.851	0.8796	0.9118	−0.1099						
					1,2-Dichloroethane (1) + Ethyl Acetate (2)						
0.1523	0.1146	24.143	0.9930	0.6631	−0.0286	0.6198	0.5958	21.071	0.9503	0.9014	−0.0690
0.2147	0.1648	23.672	0.9937	0.7313	−0.0394	0.6402	0.6182	21.015	0.9440	0.9115	−0.0678
0.2835	0.2216	23.035	0.9888	0.7864	−0.0534	0.6789	0.6640	20.940	0.9407	0.9173	−0.0640
0.3225	0.2663	22.659	0.9805	0.8416	−0.0611	0.7503	0.7445	20.822	0.9016	0.9512	−0.0562
0.4036	0.3462	22.033	0.9746	0.8614	−0.0701	0.7825	0.7796	20.772	0.8924	0.9602	−0.0526
0.4253	0.3727	21.864	0.9715	0.8709	−0.0728	0.8282	0.8319	20.734	0.8498	0.9874	−0.0459
0.5301	0.4900	21.367	0.9644	0.8845	−0.0729	0.8964	0.9005	20.706	0.8304	0.9991	−0.0350
0.5472	0.5108	21.280	0.9599	0.8909	−0.0735	0.9393	0.9445	20.762	0.8016	1.0105	−0.0249
0.5831	0.5541	21.138	0.9576	0.8950	−0.0730	0.9782	0.9814	20.806	0.7912	1.0084	−0.0159
					1-Bromo-2-chloroethane (1) + Ethyl Acetate (2)						
0.0879	0.0344	23.784	0.9991	0.9443	−0.0049	0.6367	0.4012	14.252	0.9884	0.9505	−0.0232
0.1691	0.0749	22.368	1.0002	0.9373	−0.0139	0.7260	0.5158	12.894	0.9808	0.9597	−0.0172
0.2861	0.1377	20.402	1.0023	0.9337	−0.0191	0.7487	0.5372	12.588	0.9730	0.9738	−0.0134
0.4053	0.2006	18.225	1.0045	0.9323	−0.0254	0.7691	0.5657	12.307	0.9625	0.9785	−0.0105
0.4305	0.2187	17.719	1.0070	0.9335	−0.0288	0.8086	0.6225	11.711	0.9593	0.9858	−0.0098
0.4676	0.2595	17.098	1.0055	0.9327	−0.0269	0.8449	0.6823	11.175	0.9319	1.0014	−0.0087
0.5236	0.2954	16.071	1.0030	0.9318	−0.0297	0.8784	0.7387	10.684	0.9148	1.0014	−0.0077
0.5716	0.3470	15.266	0.9980	0.9416	−0.0284	0.9144	0.8074	10.165	0.9291	1.0017	−0.0057
0.6032	0.3733	14.776	0.9940	0.9464	−0.0255						

Table 3. Coefficients A_j and Standard Deviation, σ, from Equations 1 and 2

substance + ethyl acetate (2)	A_1	A_2	A_3	A_4	$\sigma(G^E)$/J mol^{-1}
dibromomethane (1)	−0.1707	−0.0535	0.0100	0.0711	4
bromochloromethane (1)	−0.4449	−0.0536	0.0202		2
1,2-dichloroethane (1)	−0.2949	0.0117	0.0505	−0.2393	6
1-bromo-2-chloroethane (1)	−0.1122	0.0249	0.0890	−0.0283	5

Results and Discussion

The experimental vapor−liquid equilibrium data are listed in Table 2 and plotted as a function of the mole fraction in the liquid or vapor phase in Figures 1 and 2.

Excess molar Gibbs energies G_m^E were calculated by a reduction of the experimental P−x_1 data with the Redlich−Kister equation. Vapor-phase nonideality and the variation of the Gibbs energy of the pure liquid components with pressure were accounted for in terms of the molar second virial coefficients B_{ij}, estimated by the method of Tsonopoulos,[3,4] and the liquid molar volumes. The critical constants for the pure liquids were estimated by the Joback method (modification of Lydersen's method) (Reid et al.[5]).

A smoothing equation of the type

$$\frac{G^E_{\text{calcd}}}{x_1(1-x_1)RT} = \Sigma A_j(2x_1 - 1)^{j-1} \qquad (1)$$

was fit by the method of least squares. The A_j parameters, together with the standard deviations calculated as

$$\sigma(G^E) = \left\{\frac{\Sigma(G^E - G^E_{\text{calcd}})^2}{(N-n)}\right\}^{1/2} \qquad (2)$$

are given in Table 3, where N is the total number of measurements and n is the number of coefficients A_j.

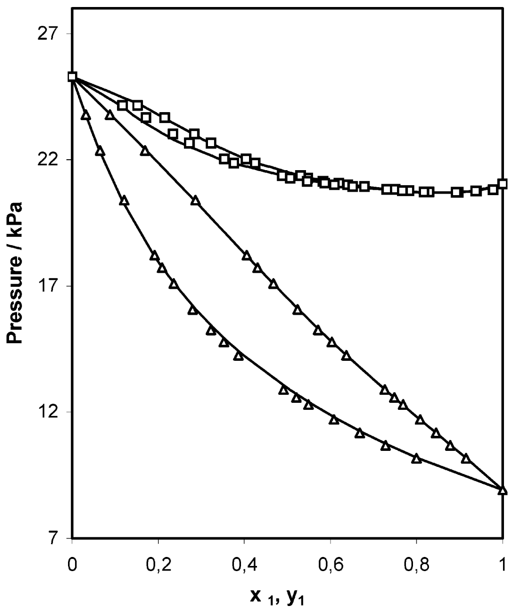

Figure 2. Vapor−liquid equilibrium diagrams at 313.15 K. Pressure, *P*, as a function of mole fraction in the liquid, x_1, or vapor, y_1, phase. Continuous curve and smoothed values, eq 1; points, direct experimental values: □, 1,2-dichloroethane (1) + ethyl acetate(2); △, 1-bromo-2-chloroethane (1) + ethyl acetate (2).

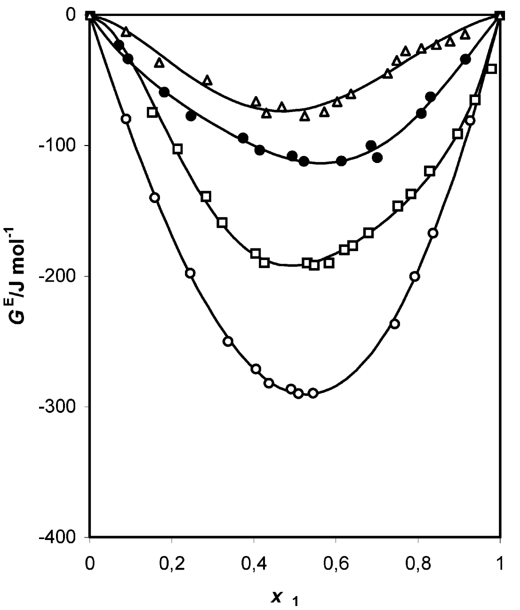

Figure 3. Excess molar Gibbs energies at 313.15 K as a function of mole fraction, x_1: ●, dibromomethane (1) + ethyl acetate (2); ○, bromochloromethane (1) + ethyl acetate (2); □, 1,2-dichloroethane (1) + ethyl acetate (2); △, 1-bromo-2-chloroethane (1) + ethyl acetate (2); —, Redlich−Kister.

Table 4. Correlation Parameters for Activity Coefficients and Average Deviation for Studied Systems

equation	A_{12}	A_{21}	ΔP/kPa	Δy_1
Dibromomethane (1) + Ethyl Acetate (2)				
Margules[a]	−0.2014	−0.0781	0.1413	0.0073
van Laar[a]	−0.2114	−0.1085	0.1267	0.0074
Wilson[b]	563.8383	−563.7740	0.1053	0.0083
NRTL[c] (α_{12} = 0.2947)	−384.6529	352.2796	0.1040	0.0086
UNIQUAC[d]	568.8001	−403.8815	0.1493	0.0094
Bromochloromethane (1) + Ethyl Acetate (2)				
Margules[a]	−0.4295	−0.4933	0.1040	0.0054
van Laar[a]	−0.4338	−0.4939	0.1067	0.0054
Wilson[b]	33.3663	−302.3565	0.1093	0.0054
NRTL[c] (α_{12} = 0.3064)	−3.6104	−266.3912	0.1067	0.0054
UNIQUAC[d]	866.9816	−567.5797	0.2053	0.0060
1,2-Dichloroethane (1) + Ethyl Acetate (2)				
Margules[a]	−0.3146	−0.2894	0.1093	0.0017
van Laar[a]	−0.3155	−0.2899	0.1093	0.0017
Wilson[b]	−542.7863	1007.2155	0.1200	0.0030
NRTL[c] (α_{12} = 0.3038)	−176.6634	−3.7375	0.1093	0.0017
UNIQUAC[d]	−249.5937	230.3217	0.1093	0.0017
1-Bromo-2-chloroethane (1) + Ethyl Acetate (2)				
Margules[a]	−0.2793	−0.0510	0.1867	0.0064
van Laar[a]	−0.3274	−0.1096	0.1813	0.0074
Wilson[b]	−509.7632	1037.3279	0.0720	0.0080
NRTL[c] (α_{12} = 0.3049)	−390.9309	355.5539	0.1360	0.0097
UNIQUAC[d]	−218.0421	218.1045	0.1293	0.0100

[a] Margules and van Laar constants (K). [b] Wilson's interaction parameters (J·mol^{-1}). [c] NRTL's interaction parameters (J·mol^{-1}). [d] UNIQUAC's interaction parameters (J·mol^{-1}).

The activity coefficients were correlated by means of the Margules, van Laar, Wilson, NRTL, and UNIQUAC equations (Table 4).

The thermodynamic consistency of the experimental data was checked by means of the test of Van Ness et al.[6] in the version of Fredenslund et al.[7] According to this test, the data are considered consistent if the average deviation in *y*, Δy, is less than 0.01. In this work, the Δy values obtained range from $\Delta y = 0.0017$ for ethyl acetate + 1,2-dichloroethane (Margules, van Laar, NRTL, UNIQUAC) to $\Delta y = 0.0100$ for ethyl acetate + 1-bromo-2-chloroethane (UNIQUAC), which shows these data to be thermodynamically consistent.

The excess molar Gibbs energies for the studied systems are plotted in Figure 3 as a function of the mole fraction of the liquid phase. The calculated excess molar Gibbs energies of all of the mixtures are negative and range from −75 J·mol^{-1} for ethyl acetate + 1-bromo-2-chloroethane to −300 J·mol^{-1} for ethyl acetate + bromochloromethane at $x = 0.5$.

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