Isothermal Vapor−Liquid Equilibria and Excess Enthalpies of (Propyl Ethanoate + Heptane), (Propyl Ethanoate + Cyclohexane), and (Propyl Ethanoate + 1-Hexene)

Latifa Negadi,*[†,‡] Aouicha Belabbaci,[†] Ahmed Ait Kaci,[§] and Jacques Jose[‡]

Department of Chemistry, Faculty of Sciences, University Aboubekr Belkaid of Tlemcen, P.O. Box 119, Tlemcen 13000, Algeria, LSSA, Laboratoire des Sciences et Stratégies Analytiques, UMR 5180, Université Claude Bernard Lyon I, 43 Boulevard du 11 Novembre 1918, Villeurbanne Cedex 69622, France, and Laboratoire de Thermodynamique des Mélanges Organiques, Université des Sciences et Technologies Houari Boumédiène, Dar El Beïda, Alger 16100, Algeria

The vapor pressures of (propyl ethanoate + heptane), (propyl ethanoate + cyclohexane), and (propyl ethanoate + 1-hexene) and of all the pure components were measured by means of a static device at temperatures between (263 and 363) K. The data were correlated with the Antoine equation. From these data, excess Gibbs functions were calculated for several constant temperatures and fitted to a fourth-order Redlich−Kister equation. All the systems show positive deviations from ideality. Additionally, molar excess enthalpies for the three binary systems of propyl ethanoate with heptane, cyclohexane, and 1-hexene at a temperaure of 298.15 K have been carried out using a C80 II (Setaram) calorimeter. The excess properties were compared with the results using the available "ester" main group of the group contribution method Modified UNIFAC (Dortmund), which is a well-known model for the prediction of phase equilibria and excess properties.

Introduction

The present paper is part of a research program on (vapor−liquid) equilibria (VLE) and excess enthalpies (H^{E}) in mixtures of strongly polar non-hydrogen-bonded compounds with saturated, unsaturated, and aromatic hydrocarbons.[1−8] VLE data for binary mixtures containing propyl ethanoate and benzene or isopropylbenzene have been reported previously.[5] The purpose of the present work is to investigate VLE and H^{E} of (propyl ethanoate + heptane), (propyl ethanoate + cyclohexane), or (propyl ethanoate + 1-hexene) with a view to use the results to determine interaction parameters for predictive group contribution methods (Modified UNIFAC (Dortmund) and DISQUAC).

A survey of the literature[9,10,12,13] shows that VLE and H^{E} data are scarce. For (propyl ethanoate + cyclohexane), there exist two references that provide VLE data. In one, Wichterle and Linek[11] report isothermal measurements at temperatures of (335.15 and 350.15) K, while a second one by Slavin and Abramzon[14] provides no numerical values. For (propyl ethanoate + heptane), Paz Andrade et al.[15] and Ortega et al.[16] have reported H^{E} measurements at $T = 298.15$ K. The isothermal VLE and G^{E} of (propyl ethanoate + heptane), (propyl ethanoate + cyclohexane), or (propyl ethanoate + 1-hexene) published by us previously[8] were used with the present measurements to provide a correlation.

Experimental Section

The substances were supplied by Aldrich Chemical Co. (Milwaukee, WI), E. Merck AG (Darmstadt, GFR), and Janssen Chimica (Geel, Belgium). Prior to use, heptane was fractionally distilled over Na. The other compounds were used without further purification. The purities, tested by GLC, were as follows: propyl ethanoate (Aldrich, ∼ 99 %), heptane (Merck, ∼ 99.9 %), cyclohexane (Janssen, > 99 %), and 1-hexene (Janssen, ∼ 99 %).

Table 1. Coefficients A, *B*, and *C* and Overall Mean Relative Deviation in Pressure of the Antoine Equation (eq 1)

compound	temperature/K	*A*	*B*	*C*	$(\delta p/p)$/%
propyl ethanoate	273.18−363.12	7.13071	1343.10	214.7950	0.09
heptane	283.33−370.89	6.97272	1307.44	221.1276	0.09
cyclohexane	283.37−373.01	6.82660	1196.41	222.3905	0.07
1-hexene	253.43−353.04	6.87274	1157.75	226.4812	0.09

$$^{a}\ (\delta p/p)/\% = \frac{1}{N}\sum_{i=1}^{n} 100\left(\frac{P_{\text{calc}} - P_{\text{exp}}}{P_{\text{exp}}}\right)$$

The experimental vapor pressure (p) data were obtained with an apparatus described in detail by Blondel-Telouk and coworkers[17,18] as a function of the temperature (T) for constant mole fraction composition (x_i). The apparatus allows measurements at pressures from (27 to 200 × 10^{3}) Pa and at temperatures from (258.15 to 468.15) K. The pressure was measured with a pressure gauge (Rosemount, model 1151 DPE 22S2, Minneapolis, MN), separated from the working fluid by a differential pressure indicator (MKS, model 615D, MKS Instruments, USA). The pressure gauges were periodically checked against a Hg or oil manometer and a Bouty (Paris, France) type 70298 cathetometer, which when combined provide pressures with an uncertainty of 1 Pa. The temperature of the oil-filled thermostat was maintained constant to ± 0.01 K. The temperature was measured by means of a copper-constantan thermocouple calibrated against a Leeds and Northrup standard platinum resistance thermometer 8163-B, calibrated by the National Bureau of Standards (Washington, DC) and connected to Mueller type G2 bridge (with a precision 10^{-4} Ω). All temperatures are reported on ITS-

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* Corresponding author. Tel/Fax: +213-43-28-65-30. E-mail: l_negadi@mail.univ-tlemcen.dz.

[†] University Aboubekr Belkaid of Tlemcen.

[‡] Université Claude Bernard Lyon I.

[§] Université des Sciences et Technologies Houari Boumédiène.

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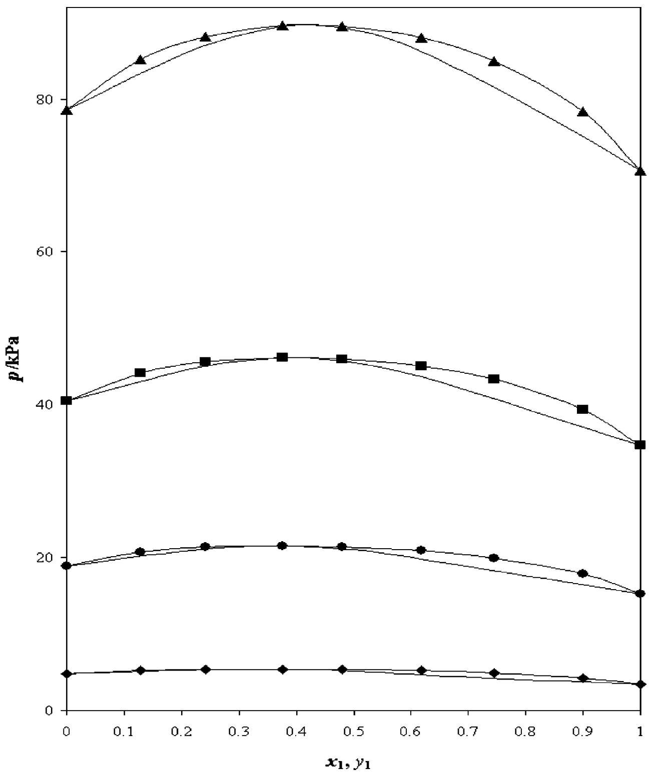

Figure 1. Experimental and calculated $p-x(y)$ behavior of the system propyl ethanoate (1) + heptane (2) at different temperatures: ◆, 293.15 K; ●, 323.15 K; ■, 343.15; ▲, 363.15 K; —, calculated values using Barker's method.

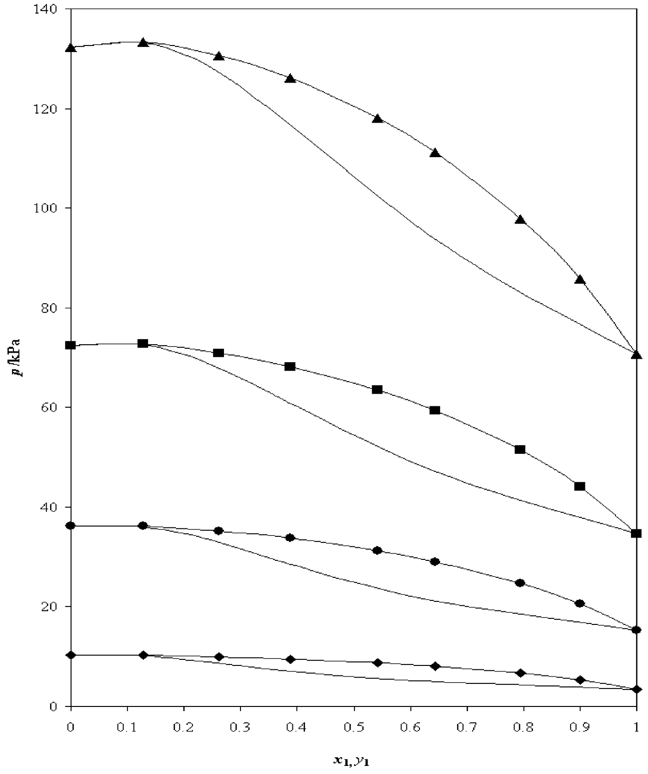

Figure 2. Experimental and calculated $p-x(y)$ behavior of the system propyl ethanoate (1) + cyclohexane (2) at different temperatures: ◆, 293.15 K; ●, 323.15 K; ■, 343.15; ▲, 363.15 K; —, calculated values using Barker's method.

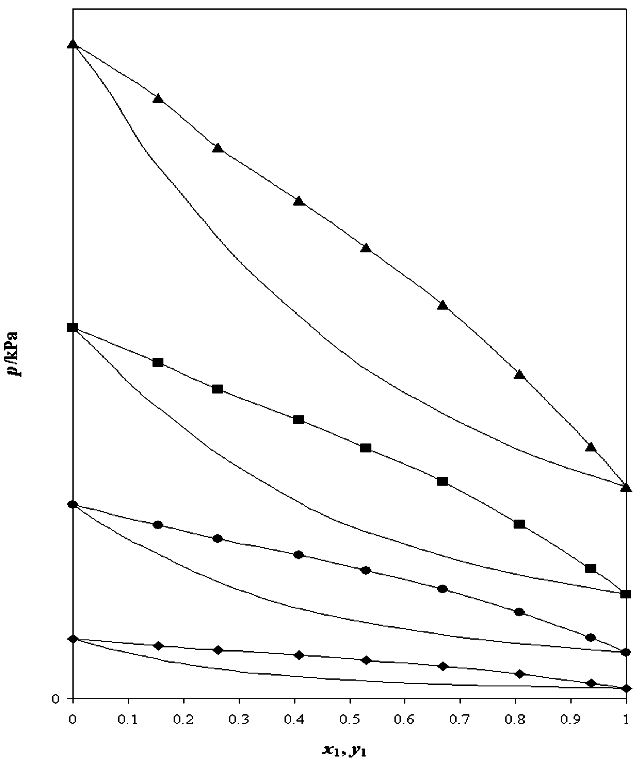

Figure 3. Experimental and calculated $p-x(y)$ behavior of the system propyl ethanoate (1) + 1-hexene (2) at different temperatures: ◆, 293.15 K; ●, 323.15 K; ■, 343.15; ▲, 363.15 K; —, calculated values using Barker's method.

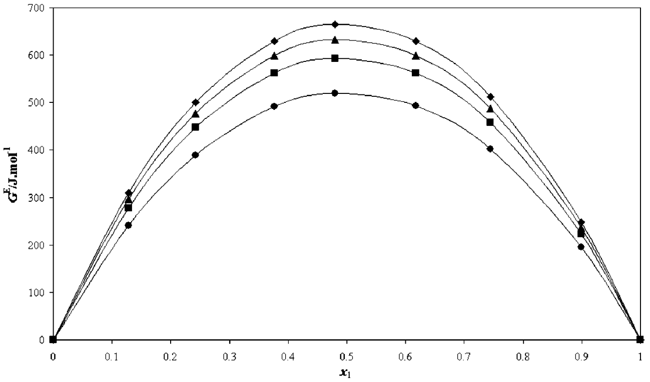

Figure 4. G^{E} against x_1 for propyl ethanoate (1) + heptane (2) system: ◆, 273.15 K; ▲, 298.15 K; ■, 323.15 K; ●, 363.15K; —, calculated values using eq 5.

90. The estimated uncertainties in pressure, temperature, and mole fraction are as follows: $\sigma(p) = 0.15(p/\mathrm{Pa})$ for $p < 13.3$ Pa, $\sigma(p) = 0.05(p/\mathrm{Pa})$ at pressure between (13.3 and 200) Pa, $\sigma(p) = 0.005(p/\mathrm{Pa})$ in the range (200 to 1000) Pa, $\sigma(p) = 0.002(p/\mathrm{Pa})$ for the range (1000 to 200 × 10^3) Pa, $\sigma(T) = 0.01$ K and $\sigma(x_i) = 0.0002$.

Mixtures were prepared by mass and thoroughly degassed by distillation as described by Blondel-Tellouk and co-workers.[17,18] The final composition of the liquid was determined after each pressure measurement by gas−liquid chromatography with a column filled with a stationary phase of Carbowax and a thermal conductivity detector.

The experimental H^{E} data were taken at atmospheric pressure by means of a microcalorimeter, model C80II (SETARAM, Lyon, France). The temperature T (ITS-90) was maintained constant at (298.15 ± 0.02) K. Measurements on (cyclohexane + heptane) differed by 2 % from values reported by Marsh[19] and verified the operation of the apparatus. The estimated uncertainties in the mole fraction composition x_i and H^{E} are, respectively, $\sigma(x_i) = 0.0002$ and $\sigma(H^{\mathrm{E}}) = 5\ \mathrm{J{\cdot}mol^{-1}}$.

Table 2. Values of the Vapor Pressure p, Standard Deviations ($\delta p/p$)/%, Activity Coefficients γ_1 and γ_2, and Excess Molar Gibbs Functions G^E for the Binary System Propyl Ethanoate (1) + Heptane (2)

x_1	y_1	p / kPa	$\delta p/p$	γ_1	γ_2	G^E / J·mol^{-1}	x_1	y_1	p / kPa	$\delta p/p$	γ_1	γ_2	G^E / J·mol^{-1}
$T = 273.15$ K													
0.0000	0.0000	1.5312	0.00	3.5382	1.0000	0.0	0.6179	0.4488	1.6523	0.03	1.1911	1.5557	628.9
0.1278	0.1891	1.6826	−0.26	2.4784	1.0240	310.3	0.7441	0.5233	1.5534	−0.18	1.0867	1.8934	511.5
0.2425	0.2740	1.7325	0.17	1.9402	1.0821	500.8	0.8996	0.6954	1.3210	0.06	1.0142	2.6136	247.9
0.3762	0.3413	1.7326	0.11	1.5589	1.1930	629.4	1.0000	1.0000	1.0061	0.00	1.0000	3.4301	0.0
0.4793	0.3860	1.7104	0.05	1.3667	1.3162	664.9							
$T = 283.15$ K													
0.0000	0.0000	2.7597	0.00	3.3191	1.0000	0.0	0.6179	0.4653	2.9988	0.05	1.1805	1.5194	617.6
0.1278	0.1900	3.0354	−0.17	2.3634	1.0228	305.1	0.7441	0.5436	2.8286	−0.11	1.0823	1.8299	502.5
0.2425	0.2781	3.1279	0.15	1.8728	1.0779	492.1	0.8996	0.7162	2.4314	0.04	1.0135	2.4860	243.7
0.3762	0.3497	3.1335	0.06	1.5223	1.1823	618.1	1.0000	1.0000	1.9091	0.00	1.0000	3.2226	0.0
0.4793	0.3978	3.0962	−0.03	1.3443	1.2973	652.9							
$T = 293.15$ K													
0.0000	0.0000	4.7364	0.00	3.1197	1.0000	0.0	0.6179	0.4803	5.1778	0.06	1.1702	1.4851	605.1
0.1278	0.1901	5.2096	−0.10	2.2573	1.0217	299.3	0.7441	0.5622	4.8996	−0.07	1.0780	1.7707	492.6
0.2425	0.2813	5.3722	0.13	1.8100	1.0739	482.3	0.8996	0.7354	4.2553	0.03	1.0129	2.3687	239.1
0.3762	0.3570	5.3914	0.03	1.4878	1.1720	605.5	1.0000	1.0000	3.4300	0.00	1.0000	3.0337	0.0
0.4793	0.4084	5.3331	−0.08	1.3230	1.2793	639.6							
$T = 298.15$ K													
0.0000	0.0000	6.1035	0.00	3.0267	1.0000	0.0	0.6179	0.4873	6.6904	0.07	1.1653	1.4688	598.5
0.1278	0.1901	6.7114	−0.08	2.2074	1.0212	296.2	0.7441	0.5708	6.3408	−0.05	1.0759	1.7427	487.3
0.2425	0.2826	6.9232	0.12	1.7803	1.0719	477.2	0.8996	0.7440	5.5345	0.02	1.0126	2.3137	236.7
0.3762	0.3603	6.9543	0.02	1.4713	1.1670	598.9	1.0000	1.0000	4.5140	0.00	1.0000	2.9457	0.0
0.4793	0.4133	6.8832	−0.10	1.3127	1.2707	632.5							
$T = 303.15$ K													
0.0000	0.0000	7.7870	0.00	2.9356	1.0000	0.0	0.6179	0.4940	8.5564	0.07	1.1605	1.4528	591.5
0.1278	0.1898	8.5578	−0.06	2.1589	1.0206	292.7	0.7441	0.5791	8.1219	−0.03	1.0738	1.7155	481.7
0.2425	0.2837	8.8306	0.11	1.7515	1.0699	471.6	0.8996	0.7520	7.1235	0.01	1.0123	2.2607	234.1
0.3762	0.3634	8.8786	0.01	1.4554	1.1619	591.8	1.0000	1.0000	5.8745	0.00	1.0000	2.8610	0.0
0.4793	0.4180	8.7934	−0.11	1.3028	1.2621	625.1							
$T = 313.15$ K													
0.0000	0.0000	12.3240	0.00	2.7659	1.0000	0.0	0.6179	0.5066	13.6017	0.07	1.1512	1.4223	577.0
0.1278	0.1891	13.5244	−0.04	2.0678	1.0195	285.6	0.7441	0.5946	12.9500	−0.02	1.0698	1.6642	470.1
0.2425	0.2856	13.9638	0.08	1.6971	1.0659	459.9	0.8996	0.7670	11.4647	0.01	1.0116	2.1612	228.6
0.3762	0.3691	14.0660	0.01	1.4251	1.1522	577.1	1.0000	1.0000	9.6450	0.00	1.0000	2.7029	0.0
0.4793	0.4267	13.9495	−0.11	1.2839	1.2456	609.6							
$T = 323.15$ K													
0.0000	0.0000	18.8540	0.00	2.6097	1.0000	0.0	0.6179	0.5181	20.8894	0.07	1.1422	1.3938	561.7
0.1278	0.1880	20.6521	−0.02	1.9837	1.0184	277.8	0.7441	0.6087	19.9467	−0.02	1.0659	1.6165	457.8
0.2425	0.2871	21.3346	0.06	1.6467	1.0620	447.5	0.8996	0.7803	17.8170	0.00	1.0110	2.0697	222.7
0.3762	0.3742	21.5312	0.01	1.3968	1.1428	561.6	1.0000	1.0000	15.2537	0.00	1.0000	2.5577	0.0
0.4793	0.4346	21.3823	−0.10	1.2660	1.2299	593.2							
$T = 333.15$ K													
0.0000	0.0000	27.9860	0.00	2.4636	1.0000	0.0	0.6179	0.5287	31.1101	0.07	1.1337	1.3669	545.6
0.1278	0.1867	30.5853	−0.02	1.9052	1.0172	269.4	0.7441	0.6216	29.7903	−0.03	1.0620	1.5721	444.8
0.2425	0.2881	31.6119	0.03	1.5997	1.0581	434.1	0.8996	0.7923	26.8360	0.01	1.0104	1.9850	216.4
0.3762	0.3788	31.9630	0.02	1.3704	1.1336	545.1	1.0000	1.0000	23.3323	0.00	1.0000	2.4236	0.0
0.4793	0.4418	31.7869	−0.08	1.2492	1.2148	576.0							
$T = 343.15$ K													
0.0000	0.0000	40.4285	0.00	2.3277	1.0000	0.0	0.6179	0.5384	45.0718	0.05	1.1255	1.3416	528.8
0.1278	0.1851	44.0717	−0.02	1.8322	1.0160	260.3	0.7441	0.6335	43.2776	−0.05	1.0583	1.5308	431.2
0.2425	0.2889	45.5720	0.01	1.5561	1.0542	419.9	0.8996	0.8032	39.3018	0.02	1.0097	1.9065	209.7
0.3762	0.3829	46.1634	0.03	1.3457	1.1247	527.8	1.0000	1.0000	34.6401	0.00	1.0000	2.2996	0.0
0.4793	0.4485	45.9752	−0.05	1.2333	1.2003	558.1							
$T = 353.15$ K													
0.0000	0.0000	56.9935	0.00	2.2010	1.0000	0.0	0.6179	0.5473	63.7000	0.04	1.1176	1.3178	511.4
0.1278	0.1834	61.9596	−0.03	1.7642	1.0148	250.7	0.7441	0.6444	61.3250	−0.08	1.0546	1.4924	417.0
0.2425	0.2894	64.0963	−0.01	1.5154	1.0502	405.0	0.8996	0.8131	56.1215	0.04	1.0091	1.8338	202.7
0.3762	0.3866	65.0462	0.05	1.3227	1.1159	509.8	1.0000	1.0000	50.0674	0.00	1.0000	2.1845	0.0
0.4793	0.4545	64.8746	−0.01	1.2184	1.1865	539.4							
$T = 363.15$ K													
0.0000	0.0000	78.5915	0.00	2.0828	1.0000	0.0	0.6179	0.5556	88.0338	0.02	1.1101	1.2954	493.5
0.1278	0.1816	85.1933	−0.03	1.7008	1.0136	240.5	0.7441	0.6543	84.9662	−0.11	1.0510	1.4565	402.2
0.2425	0.2897	88.1663	−0.02	1.4775	1.0463	389.4	0.8996	0.8220	78.3294	0.07	1.0085	1.7661	195.3
0.3762	0.3899	89.6324	0.07	1.3011	1.1074	491.1	1.0000	1.0000	70.6374	0.00	1.0000	2.0775	0.0
0.4793	0.4601	89.5249	0.02	1.2043	1.1732	520.2							

Table 3. Values of the Vapor Pressure *p*, Standard Deviations ($\delta p/p$)/%, Activity Coefficients γ_1 and γ_2, and Excess Molar Gibbs Functions G^E for the Binary System Propyl Ethanoate (1) + Cyclohexane (2)

		p				G^E			p				G^E
x_1	y_1	kPa	$\delta p/p$	γ_1	γ_2	J·mol^{-1}	x_1	y_1	kPa	$\delta p/p$	γ_1	γ_2	J·mol^{-1}
T = 263.15 K													
0.0000	0.0000	2.0818	0.00	1.4959	1.0000	0.0	0.6437	0.2291	1.6032	0.08	1.1422	1.6659	585.2
0.1288	0.0847	2.0551	0.28	2.6969	1.0343	343.9	0.7938	0.3187	1.3030	−0.07	1.0492	2.0715	412.0
0.2626	0.1246	1.9753	−0.11	1.8781	1.1279	556.3	0.9004	0.4645	0.9786	0.02	1.0123	2.5302	226.4
0.3875	0.1529	1.8905	−0.10	1.4950	1.2576	648.1	1.0000	1.0000	0.4981	0.00	1.0000	3.2139	0.0
0.5425	0.1931	1.7419	0.02	1.2412	1.4762	646.3							
T = 273.15 K													
0.0000	0.0000	3.7302	0.00	4.0670	1.0000	0.0	0.6437	0.2563	2.8750	0.03	1.1339	1.6098	568.9
0.1288	0.0893	3.6899	0.21	2.5249	1.0320	333.2	0.7938	0.3556	2.3553	−0.03	1.0467	1.9767	401.3
0.2626	0.1345	3.5515	−0.09	1.8025	1.1186	539.1	0.9004	0.5088	1.8040	0.01	1.0117	2.3898	220.9
0.3875	0.1679	3.3950	−0.08	1.4577	1.2379	628.5	1.0000	1.0000	1.0061	0.00	1.0000	3.0018	0.0
0.5425	0.2150	3.1239	0.04	1.2256	1.4374	627.7							
T = 283.15 K													
0.0000	0.0000	6.3567	0.00	3.7116	1.0000	0.0	0.6437	0.2824	4.9187	−0.01	1.1255	1.5607	552.5
0.1288	0.0935	6.3012	0.16	2.3778	1.0298	322.9	0.7938	0.3906	4.0626	0.00	1.0439	1.8929	390.1
0.2626	0.1440	6.0747	−0.07	1.7358	1.1104	522.7	0.9004	0.5492	3.1700	0.00	1.0110	2.2637	214.9
0.3875	0.1823	5.8045	−0.07	1.4237	1.2205	609.6	1.0000	1.0000	1.9091	0.00	1.0000	2.8074	0.0
0.5425	0.2360	5.3401	0.04	1.2106	1.4036	609.2							
T = 293.15 K													
0.0000	0.0000	10.3663	0.00	3.4135	1.0000	0.0	0.6437	0.3072	8.0727	−0.02	1.1172	1.5174	536.0
0.1288	0.0975	10.2981	0.13	2.2507	1.0279	313.1	0.7938	0.4234	6.7227	0.02	1.0411	1.8184	378.5
0.2626	0.1530	9.9453	−0.05	1.6766	1.1029	506.8	0.9004	0.5858	5.3382	−0.01	1.0103	2.1503	208.5
0.3875	0.1960	9.5046	−0.06	1.3925	1.2051	591.2	1.0000	1.0000	3.4300	0.00	1.0000	2.6310	0.0
0.5425	0.2561	8.7504	0.04	1.1962	1.3737	590.9							
T = 298.15 K													
0.0000	0.0000	13.0432	0.00	3.2820	1.0000	0.0	0.6437	0.3191	10.1971	−0.03	1.1132	1.4976	527.8
0.1288	0.0994	12.9713	0.12	2.1935	1.0270	308.3	0.7938	0.4390	8.5268	0.02	1.0397	1.7842	372.6
0.2626	0.1573	12.5385	−0.04	1.6494	1.0995	499.1	0.9004	0.6027	6.8279	−0.01	1.0100	2.0982	205.2
0.3875	0.2027	11.9862	−0.06	1.3780	1.1980	582.2	1.0000	1.0000	4.5140	0.00	1.0000	2.5495	0.0
0.5425	0.2658	11.0420	0.04	1.1893	1.3600	581.9							
T = 303.15 K													
0.0000	0.0000	16.2626	0.00	3.1605	1.0000	0.0	0.6437	0.3308	12.7688	−0.03	1.1092	1.4789	519.6
0.1288	0.1012	16.1904	0.10	2.1400	1.0261	303.5	0.7938	0.4540	10.7211	0.03	1.0383	1.7519	366.7
0.2626	0.1615	15.6650	−0.03	1.6237	1.0962	491.5	0.9004	0.6187	8.6552	−0.02	1.0096	2.0488	201.8
0.3875	0.2091	14.9806	−0.06	1.3641	1.1912	573.4	1.0000	1.0000	5.8745	0.00	1.0000	2.4724	0.0
0.5425	0.2753	13.8113	0.04	1.1827	1.3471	573.0							
T = 313.15 K													
0.0000	0.0000	24.6518	0.00	2.9438	1.0000	0.0	0.6437	0.3531	19.5422	−0.03	1.1017	1.4443	503.3
0.1288	0.1047	24.5949	0.09	2.0427	1.0244	294.3	0.7938	0.4825	16.5426	0.03	1.0356	1.6924	354.9
0.2626	0.1696	23.8428	−0.02	1.5763	1.0900	476.6	0.9004	0.6481	13.5660	−0.01	1.0090	1.9581	195.1
0.3875	0.2216	22.8243	−0.06	1.3381	1.1786	555.9	1.0000	1.0000	9.6451	0.00	1.0000	2.3313	0.0
0.5425	0.2935	21.0837	0.04	1.1700	1.3231	555.3							
T = 323.15 K													
0.0000	0.0000	36.2446	0.00	2.7561	1.0000	0.0	0.6437	0.3742	29.0388	−0.01	1.0947	1.4130	487.4
0.1288	0.1080	36.2374	0.08	1.9564	1.0229	285.2	0.7938	0.5088	24.7798	0.01	1.0331	1.6390	343.2
0.2626	0.1773	35.1985	−0.02	1.5335	1.0843	462.0	0.9004	0.6743	20.6249	−0.01	1.0083	1.8774	188.6
0.3875	0.2336	33.7387	−0.06	1.3144	1.1671	538.9	1.0000	1.0000	15.2538	0.00	1.0000	2.2071	0.0
0.5425	0.3109	31.2392	0.04	1.1584	1.3013	538.1							
T = 333.15 K													
0.0000	0.0000	51.8539	0.00	2.5925	1.0000	0.0	0.6437	0.3943	42.0198	0.01	1.0883	1.3844	471.9
0.1288	0.1111	51.9512	0.07	1.8793	1.0215	276.4	0.7938	0.5331	36.1408	−0.01	1.0309	1.5908	332.0
0.2626	0.1847	50.5621	−0.02	1.4947	1.0790	447.7	0.9004	0.6976	30.5072	0.00	1.0077	1.8058	182.3
0.3875	0.2451	48.5387	−0.06	1.2927	1.1564	522.2	1.0000	1.0000	23.3324	0.00	1.0000	2.0993	0.0
0.5425	0.3276	45.0628	0.03	1.1478	1.2812	521.2							
T = 343.15 K													
0.0000	0.0000	72.3903	0.00	2.4486	1.0000	0.0	0.6437	0.4134	59.3637	0.03	1.0827	1.3579	456.9
0.1288	0.1140	72.6733	0.07	1.8098	1.0202	267.7	0.7938	0.5556	51.4538	−0.04	1.0289	1.5472	321.4
0.2626	0.1917	70.8708	−0.02	1.4592	1.0741	433.6	0.9004	0.7182	44.0172	0.02	1.0072	1.7426	176.4
0.3875	0.2561	68.1491	−0.07	1.2730	1.1465	505.7	1.0000	1.0000	34.6401	0.00	1.0000	2.0068	0.0
0.5425	0.3435	63.4530	0.03	1.1383	1.2625	504.7							
T = 353.15 K													
0.0000	0.0000	98.8545	0.00	2.3217	1.0000	0.0	0.6437	0.4316	82.0656	0.06	1.0779	1.3330	442.5
0.1288	0.1167	99.4373	0.07	1.7467	1.0190	259.0	0.7938	0.5764	71.6687	−0.08	1.0274	1.5076	311.5
0.2626	0.1984	97.1622	−0.03	1.4266	1.0696	419.6	0.9004	0.7365	62.0938	0.04	1.0069	1.6871	171.0
0.3875	0.2666	93.5996	−0.07	1.2549	1.1371	489.4	1.0000	1.0000	50.0676	0.00	1.0000	1.9288	0.0
0.5425	0.3589	87.4188	0.03	1.1298	1.2448	488.5							
T = 363.15 K													
0.0000	0.0000	132.3272	0.00	2.2093	1.0000	0.0	0.6437	0.4489	111.2333	0.10	1.0739	1.3094	428.6
0.1288	0.1192	133.3636	0.07	1.6889	1.0179	250.5	0.7938	0.5957	97.8571	−0.14	1.0262	1.4713	302.4
0.2626	0.2047	130.5664	−0.04	1.3963	1.0653	405.5	0.9004	0.7526	85.8134	0.07	1.0066	1.6385	166.4
0.3875	0.2767	126.0174	−0.08	1.2383	1.1281	473.1	1.0000	1.0000	70.6376	0.00	1.0000	1.8643	0.0
0.5425	0.3737	118.0743	0.04	1.1224	1.2279	472.7							

Table 4. Values of the Vapor Pressure p, Standard Deviations $(\delta p/p)$/%, Activity Coefficients γ_1 and γ_2, and Excess Molar Gibbs Functions G^E for the Binary System Propyl Ethanoate (1) + 1-Hexene (2)

x_1	y_1	p/kPa	$\delta p/p$	γ_1	γ_2	G^E/J·mol^{-1}	x_1	y_1	p/kPa	$\delta p/p$	γ_1	γ_2	G^E/J·mol^{-1}
T = 273.15 K													
0.0000	0.0000	7.6868	0.00	1.7481	1.0000	0.0	0.6682	0.1777	4.0652	0.38	1.0656	1.3106	300.2
0.1540	0.3509	6.8002	−0.18	1.5288	1.0117	170.8	0.8082	0.2768	2.9943	−0.39	1.0200	1.4818	207.6
0.2625	0.0593	6.2226	−0.31	1.3908	1.0373	258.1	0.9362	0.5372	1.7626	0.19	1.0020	1.6705	78.6
0.4090	0.0932	5.5228	0.38	1.2376	1.1006	326.7	1.0000	1.0000	1.0061	0.00	1.0000	1.7727	0.0
0.5290	0.1255	4.8634	−0.25	1.1427	1.1811	338.3							
T = 283.15 K													
0.0000	0.0000	12.6450	0.00	1.6497	1.0000	0.0	0.6682	0.2020	6.7717	0.33	1.0619	1.2907	293.9
0.1540	0.0394	11.1823	−0.39	1.4859	1.0094	162.3	0.8082	0.3109	5.0526	−0.41	1.0184	1.4515	202.9
0.2625	0.0673	10.2703	−0.25	1.3674	1.0319	248.0	0.9362	0.5803	3.0963	0.23	1.0018	1.6209	76.8
0.4090	0.1063	9.1266	0.39	1.2267	1.0906	317.3	1.0000	1.0000	1.9091	0.00	1.0000	1.7073	0.0
0.5290	0.1432	8.0645	−0.17	1.1363	1.1670	330.3							
T = 293.15 K													
0.0000	0.0000	19.9770	0.00	1.5725	1.0000	0.0	0.6682	0.2267	10.8400	0.29	1.0598	1.2702	288.0
0.1540	0.0437	17.6800	−0.55	1.4463	1.0078	154.5	0.8082	0.3444	8.1970	−0.50	1.0177	1.4229	199.5
0.2625	0.0752	16.2736	−0.31	1.3439	1.0276	238.1	0.9362	0.6178	5.2336	0.31	1.0017	1.5831	75.3
0.4090	0.1196	14.5059	0.45	1.2159	1.0815	307.7	1.0000	1.0000	3.4300	0.00	1.0000	1.6639	0.0
0.5290	0.1613	12.8548	−0.06	1.1309	1.1531	322.1							
T = 298.15 K													
0.0000	0.0000	24.7696	0.00	1.5365	1.0000	0.0	0.6682	0.2387	13.5350	0.27	1.0581	1.2609	284.2
0.1540	0.0458	21.9475	−0.55	1.4278	1.0070	150.5	0.8082	0.3607	10.3020	−0.49	1.0171	1.4085	196.8
0.2625	0.0792	20.2170	−0.30	1.3326	1.0256	233.1	0.9362	0.6355	6.6974	0.32	1.0016	1.5608	74.1
0.4090	0.1262	18.0399	0.45	1.2100	1.0774	302.5	1.0000	1.0000	4.5141	0.00	1.0000	1.6360	0.0
0.5290	0.1701	16.0126	−0.04	1.1275	1.1470	317.4							
T = 303.15 K													
0.0000	0.0000	30.4560	0.00	1.5033	1.0000	0.0	0.6682	0.2507	16.7614	0.25	1.0563	1.2517	280.0
0.1540	0.0479	27.0266	−0.52	1.4099	1.0062	146.6	0.8082	0.3766	12.8409	−0.48	1.0164	1.3942	193.8
0.2625	0.0831	24.9090	−0.30	1.3214	1.0238	228.1	0.9362	0.6523	8.4932	0.32	1.0015	1.5387	72.8
0.4090	0.1327	22.2497	0.43	1.2041	1.0736	297.2	1.0000	1.0000	5.8745	0.00	1.0000	1.6083	0.0
0.5290	0.1790	19.7816	−0.03	1.1239	1.1411	213.5							
T = 313.15 K													
0.0000	0.0000	44.9850	0.00	1.4454	1.0000	0.0	0.6682	0.2743	25.1220	0.22	1.0526	1.2341	270.8
0.1540	0.0522	40.0748	−0.39	1.3764	1.0050	139.1	0.8082	0.4077	19.4952	−0.43	1.0151	1.3660	187.2
0.2625	0.0909	36.9528	−0.29	1.2993	1.0207	218.2	0.9362	0.6832	13.3175	0.29	1.0013	1.4956	70.1
0.4090	0.1456	33.0750	0.39	1.1918	1.0668	286.3	1.0000	1.0000	9.6451	0.00	1.0000	1.5551	0.0
0.5290	0.1964	29.5025	−0.03	1.1165	1.1302	301.9							
T = 323.15 K													
0.0000	0.0000	64.5960	0.00	1.3977	1.0000	0.0	0.6682	0.2975	36.6153	0.20	1.0489	1.2170	260.8
0.1540	0.0564	57.8222	−0.19	1.3454	1.0041	132.2	0.8082	0.4374	28.7757	−0.36	1.0138	1.3384	180.0
0.2625	0.0985	53.3092	−0.29	1.2775	1.0182	208.5	0.9362	0.7107	20.2487	0.25	1.0012	1.4545	67.2
0.4090	0.1583	47.8092	0.31	1.1791	1.0609	274.9	1.0000	1.0000	15.2538	0.00	1.0000	1.5057	0.0
0.5290	0.2136	42.7845	−0.04	1.1089	1.1202	290.5							
T = 333.15 K													
0.0000	0.0000	90.4420	0.00	1.3593	1.0000	0.0	0.6682	0.3201	52.0460	0.19	1.0454	1.2004	250.0
0.1540	0.0605	81.4055	0.06	1.3168	1.0036	125.8	0.8082	0.4658	41.4084	−0.28	1.0127	1.3116	172.4
0.2625	0.1060	75.0005	−0.31	1.2561	1.0164	199.0	0.9362	0.7351	29.9447	0.19	1.0011	1.4162	64.3
0.4090	0.1706	67.3912	0.22	1.1661	1.0559	263.1	1.0000	1.0000	23.3324	0.00	1.0000	1.4613	0.0
0.5290	0.2304	60.5036	−0.06	1.1012	1.1108	278.4							
T = 343.15 K													
0.0000	0.0000	123.7880	0.00	1.3293	1.0000	0.0	0.6682	0.3422	72.3065	0.20	1.0421	1.1840	238.5
0.1540	0.0646	112.0949	0.33	1.2900	1.0034	120.0	0.8082	0.4928	58.2322	−0.20	1.0119	1.2854	164.7
0.2625	0.1132	103.1610	−0.34	1.2348	1.0152	189.8	0.9362	0.7566	43.1868	0.11	1.0010	1.3809	61.5
0.4090	0.1826	92.8661	0.11	1.1528	1.0516	250.8	1.0000	1.0000	34.6401	0.00	1.0000	1.4225	0.0
0.5290	0.2468	83.6406	−0.09	1.0935	1.1021	265.4							
T = 353.15 K													
0.0000	0.0000	165.9940	0.00	1.3073	1.0000	0.0	0.6682	0.3638	98.4164	0.21	1.0392	1.1677	226.5
0.1540	0.0687	151.2853	0.61	1.2651	1.0035	114.9	0.8082	0.5185	80.1985	−0.12	1.0113	1.2600	156.9
0.2625	0.1201	139.0269	−0.38	1.2137	1.0147	180.8	0.9362	0.7757	60.8843	0.03	1.0010	1.3491	58.9
0.4090	0.1941	125.3762	−0.01	1.1394	1.0480	238.2	1.0000	1.0000	50.0676	0.00	1.0000	1.3897	0.0
0.5290	0.2628	113.2747	−0.11	1.0858	1.0937	251.8							
T = 363.15 K													
0.0000	0.0000	218.5010	0.00	1.2925	1.0000	0.0	0.6682	0.3850	131.4720	0.24	1.0367	1.1515	214.0
0.1540	0.0726	200.4853	0.90	1.2416	1.0039	110.5	0.8082	0.5429	108.3694	−0.05	1.0111	1.2352	149.2
0.2625	0.1268	183.9246	−0.44	1.1927	1.0147	172.2	0.9362	0.7925	84.0764	−0.05	1.0011	1.3207	56.6
0.4090	0.2053	166.1514	−0.13	1.1259	1.0451	225.1	1.0000	1.0000	70.6376	0.00	1.0000	1.3631	0.0
0.5290	0.2784	150.5741	−0.13	1.0783	1.0858	237.5							

Table 5. Coefficients G_j and Standard Deviations σ/kPa for Least-Squares Representations by Equation 1

T/K	G_1	σ	G_2	σ	G_3	σ
Propyl Ethanoate (1) + Heptane (2)						
273.15	1.17237	(0.003)	−0.01551	(0.008)	0.07573	(0.017)
283.15	1.11049	(0.003)	−0.01476	(0.006)	0.07446	(0.012)
293.15	1.05073	(0.002)	−0.01397	(0.005)	0.07303	(0.010)
298.15	1.02170	(0.002)	−0.01357	(0.004)	0.07221	(0.009)
303.15	0.99302	(0.002)	−0.01286	(0.004)	0.07102	(0.009)
313.15	0.93749	(0.002)	−0.01153	(0.004)	0.06836	(0.008)
323.15	0.88417	(0.001)	−0.01006	(0.003)	0.06501	(0.007)
333.15	0.83279	(0.001)	−0.00818	(0.003)	0.06064	(0.006)
343.15	0.78340	(0.001)	−0.00608	(0.002)	0.05540	(0.006)
353.15	0.73588	(0.001)	−0.00376	(0.003)	0.04925	(0.006)
363.15	0.69016	(0.002)	−0.00127	(0.004)	0.04227	(0.009)
Propyl Ethanoate (1) + Cyclohexane (2)						
263.15	1.20352	(0.002)	−0.16784	(0.004)	0.13180	(0.009)
273.15	1.12550	(0.002)	−0.15184	(0.003)	0.12556	(0.007)
283.15	1.05359	(0.001)	−0.13960	(0.003)	0.11829	(0.005)
293.15	0.98712	(0.001)	−0.13019	(0.002)	0.11043	(0.005)
298.15	0.95577	(0.001)	−0.12628	(0.002)	0.10640	(0.005)
303.15	0.92560	(0.001)	−0.12278	(0.002)	0.10236	(0.004)
313.15	0.86858	(0.001)	−0.11664	(0.002)	0.09447	(0.004)
323.15	0.81567	($<10^{-3}$)	−0.11106	(0.002)	0.08709	(0.004)
333.15	0.76648	($<10^{-3}$)	−0.10551	(0.002)	0.08061	(0.004)
343.15	0.72063	(0.001)	−0.09949	(0.002)	0.07540	(0.005)
353.15	0.67773	(0.001)	−0.09270	(0.003)	0.07185	(0.006)
363.15	0.63745	(0.002)	−0.08490	(0.004)	0.07033	(0.009)
Propyl Ethanoate (1) + 1-Hexene (2)						
273.15	0.59746	(0.005)	0.00698	(0.010)	−0.03193	(0.016)
283.15	0.56224	(0.006)	0.01718	(0.010)	−0.04449	(0.018)
293.15	0.52894	0.007)	0.02825	(0.013)	−0.04805	(0.022)
298.15	0.51229	(0.007)	0.03135	(0.013)	−0.05141	(0.023)
303.15	0.49581	(0.007)	0.03376	(0.013)	−0.05436	(0.022)
313.15	0.46350	(0.006)	0.03659	(0.012)	−0.05853	(0.020)
323.15	0.43204	(0.005)	0.03724	(0.010)	−0.05999	(0.017)
333.15	0.40143	(0.004)	0.03619	(0.008)	−0.05828	(0.015)
343.15	0.37162	(0.005)	0.03386	(0.009)	−0.05307	(0.017)
353.15	0.34258	(0.007)	0.03057	(0.0013)	−0.04406	(0.023)
363.15	0.31425	(0.009)	0.02659	(0.018)	−0.03106	(0.033)

Table 6. Experimental Excess Molar Enthalpies at T = 298.15 K

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
Propyl Ethanoate (1) + Heptane (2)					
0.1087	504.3	0.5004	1144.	0.6544	1021.
0.1348	599.0	0.5217	1136.	0.7495	845.6
0.2399	893.7	0.5427	1128.	0.8346	628.3
0.3594	1084.	0.5634	1115.	0.9200	337.8
0.4570	1142.	0.5838	1098.	0.9526	207.2
Propyl Ethanoate (1) + Cyclohexane (2)					
0.1031	531.8	0.4249	1122.	0.5827	1053.
0.1888	813.9	0.4667	1124.	0.6881	900.0
0.2926	1021.	0.4876	1119.	0.7883	682.4
0.3829	1107.	0.5084	1110.	0.8945	377.1
Propyl Ethanoate (1) + 1-Hexene (2)					
0.0943	259.2	0.4822	634.9	0.6178	581.1
0.2122	475.3	0.5032	632.9	0.7186	488.9
0.3238	589.7	0.5241	627.8	0.8117	365.6
0.4180	630.6	0.5449	620.2	0.9076	198.8
0.4609	636.7				

Results and Discussion

The experimental vapor pressure data were fitted to the Antoine equation:

$$\log_{10} P(\text{mmHg}) = A - \frac{B}{C + t/°\text{C}} \tag{1}$$

The objective function Q was the sum of the squared relative deviations in pressure:

$$Q = \sum\left(\frac{P_{\text{calc}} - P_{\text{exp}}}{P_{\text{exp}}}\right)^2 \tag{2}$$

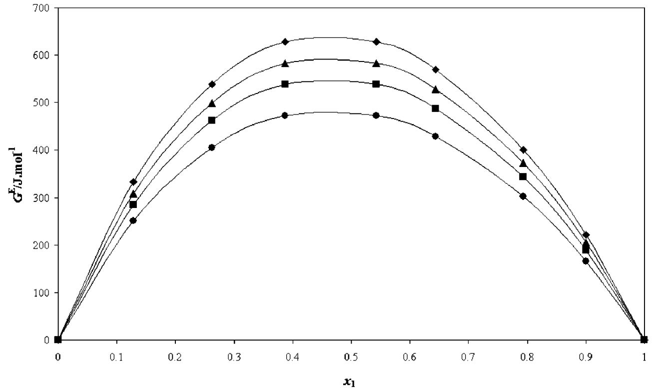

Figure 5. G^E against x_1 for propyl ethanoate (1) + cyclohexane (2) system: ◆, 273.15 K; ▲, 298.15 K; ■, 323.15 K; ●, 363.15K; —, calculated values using eq 5.

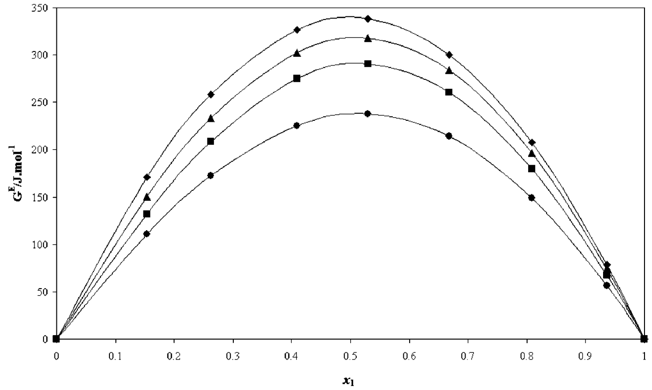

Figure 6. G^E against x_1 for propyl ethanoate (1) + 1-hexene (2) system: ◆, 273.15 K; ▲, 298.15 K; ■, 323.15 K; ●, 363.15K; —, calculated values using eq 5.

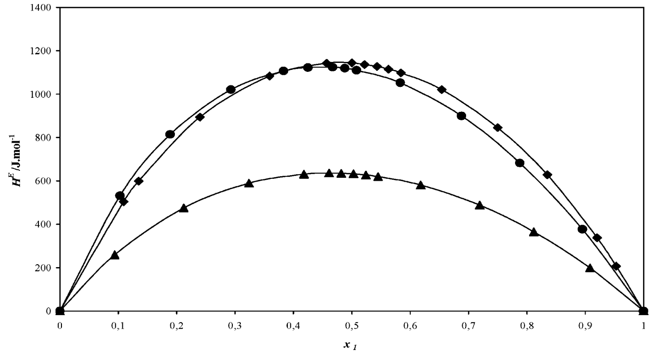

Figure 7. Experimental excess molar enthalpy H^E as a function of the mole fraction x_1 of propyl ethanoate at 298.15 K: ◆, propyl ethanoate (1) + heptane (2); ●, propyl ethanoate (1) + cyclohexane (2); ▲, propyl ethanoate (1) + 1-hexene (2); —, calculated values using eq 6.

The overall mean relative deviation in pressure is

$$\frac{\delta P}{P}/\% = \frac{100}{N}\sum\left(\frac{P_{\text{calc}} - P_{\text{exp}}}{P_{\text{exp}}}\right) \tag{3}$$

where N, the total number of experimental values, is less than 0.1 %.

Table 1 lists for the pure components propyl ethanoate, heptane, cyclohexane, and 1-hexene the temperature range; the coefficients A, B, and C of the Antoine equation; and the overall mean relative deviation in pressure.

For pure propyl ethanoate, our vapor pressure data agree to within 0.3 % with those reported in the literature by Mertl

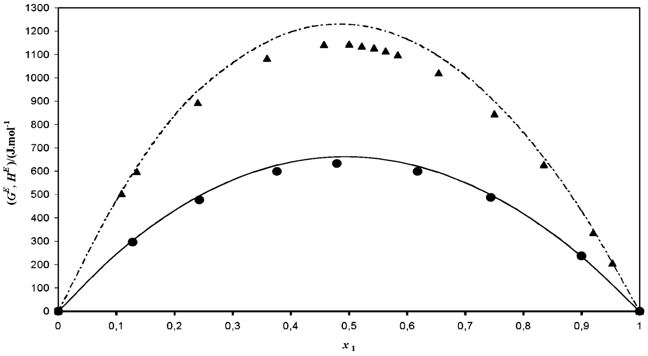

Figure 8. G^E and H^E against x_1 values for the propyl ethanoate (1) + heptane (2) binary system at 298.15 K : ●, experimental G^E; —, predicted G^E using Modified UNIFAC (Dortmund); ▲, experimental H^E; - - -, predicted H^E using Modified UNIFAC (Dortmund).

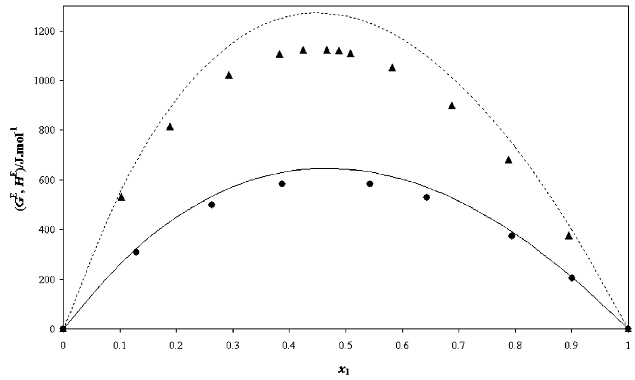

Figure 9. G^E and H^E against x_1 values for the propyl ethanoate (1) + cyclohexane (2) binary system at 298.15 K: ●, experimental G^E; —, predicted G^E using Modified UNIFAC (Dortmund); ▲, experimental H^E; - - -, predicted H^E using Modified UNIFAC (Dortmund).

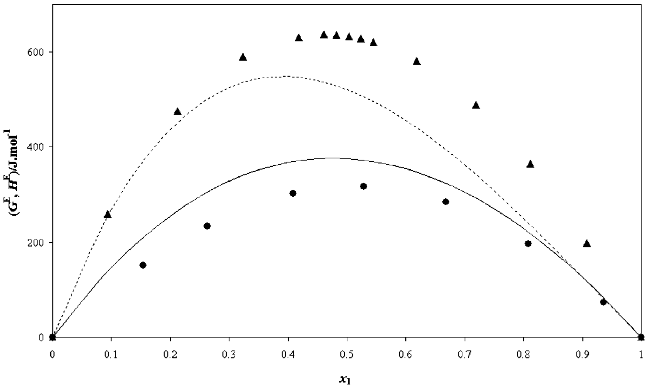

Figure 10. G^E and H^E against x_1 values for the propyl ethanoate (1) + 1-hexene (2) binary system at 298.15 K: ●, experimental G^E; —, predicted G^E using Modified UNIFAC (Dortmund); ▲, experimental H^E; - - -, predicted H^E using Modified UNIFAC (Dortmund).

and Polak[20] in the temperature range (313 to 363) K. For pure heptane, cyclohexane, and 1-hexene, our vapor pressure data agree with those reported in the literature.[21] The vapor pressure as a function of the mole fraction for each binary, shown in Figures 1 to 3, are also listed in Tables 2 through 4.

For the three binary mixtures, the vapor pressures were measured at temperatures between (263.15 and 353.15) K, and the results were fitted to the Antoine equation. The molar excess Gibbs functions G^E were estimated from the Redlich−Kister equation with the method of Barker:[22]

$$G^E = x_1(1 - x_1) \sum_{j=1}^{m} RTG_j(2x_1 - 1)^{j-1} \tag{4}$$

where x_1 is the molar fraction for propyl ethanoate. The coefficients G_j were determined by regression through minimization of the sum of deviations in pressure. Vapor-phase imperfection and variation of Gibbs function of the pure liquid components with pressure were accounted for in terms of the second molar virial coefficients, estimated by the method of Tsonopoulos,[23,24] and the molar volumes under saturation pressure.

Tables 5 to 7 also list for (propyl ethanoate + heptane), (propyl ethanoate + cyclohexane), or (propyl ethanoate + 1-hexene) the corresponding compositions of the liquid and vapor phases, the activity coefficients γ_1 and γ_2, and the values of the excess molar Gibbs functions G^E calculated by Barker's method, using the Redlich−Kister equation. (Propyl ethanoate + heptane) and (propyl ethanoate + cyclohexane) show maximum azeotropic behavior over the whole temperature range. The azeotropic compositions vary from 0.3000 to 0.4000 for (propyl ethanoate + heptane) and from 0.0350 to 0.0950 for (propyl ethanoate + cyclohexane).

For each system, the molar excess Gibbs functions G^E at different temperatures, calculated from our vapor pressure data, are plotted in Figures 4 to 6 against the mole fraction x_1 of propyl ethanoate. For (propyl ethanoate + cyclohexane), the molar excess Gibbs functions calculated from our vapor pressure data are in good agreement with those estimated by Wichterle[11] at temperatures of (335.15 and 350.15) K. For (propyl ethanoate + heptane) and (propyl ethanoate + 1-hexene), no comparisons were possible.

All binary mixtures exhibit positive deviations in G^E values calculated from the vapor pressure data. Mixtures containing saturated hydrocarbons have the largest G^E, 626 J•mol^{-1} for heptane and 583 J•mol^{-1} for cyclohexane; the G^E value decreases to ca. 312 J•mol^{-1} for 1-hexene (all G^E values are at 303.15 K).

The equimolar G^E of (propyl ethanoate + heptane) decreases with increasing temperature from 666 J•mol^{-1} at $T = 273.15$ K to 521 J•mol^{-1} at $T = 363.15$ K. The equimolar G^E of (propyl ethanoate + cyclohexane) decreases with increasing temperature from 658 J•mol^{-1} at $T = 263.15$ K to 481 J•mol^{-1} $T = 363.15$ K. The. equimolar G^E of (propyl ethanoate + 1-hexene) decreases with increasing temperature from 339 J•mol^{-1} at $T = 273.15$ K to 237 J•mol^{-1} at $T = 363.15$ K.

The experimental molar excess enthalpies H^E of the three binary mixtures have been fitted to the smoothing equation:

$$H^E_{i,\mathrm{exp}} = x_{1(1-x1)} \sum_{i=0}^{n-1} H_i(2x_1 - 1)^i \tag{5}$$

The values of the coefficients H_i and the standard deviations $\sigma(H^E)$ are given by

Table 7. Redlich−Kister Parameters (eq 5)

component 1	component 2	T/K	H_1	H_2	H_3	H_4	$\sigma(H^E)$/J•mol^{-1}
propyl ethanoate	heptane	298.15	4569.2	−345.1	518.6	−78.6	0.1
propyl ethanoate	cyclohexane	298.15	4447.4	−855.3	667.1	−377.4	0.2
propyl ethanoate	1-hexene	298.15	2531.1	−356.1	273.6	−80.8	0.1

$$\sigma(H^{\mathrm{E}}) = [\sum_{i=1}^{N} (H^{\mathrm{E}}_{i,\mathrm{exp}} - H^{\mathrm{E}}_{i,\mathrm{calc}})^2/(N-n)]^{1/2} \qquad (6)$$

where N is the number of experimental points and n is the number of coefficients H_i; they are determined by least-square analysis.

For (propyl ethanoate + heptane), the excess enthalpies H^{E} are 8 % lower than those reported by Paz Andrade et al.[15] but differ by 2 % from those reported by Ortega et al.[16] at $T = 298.15$ K. The molar excess enthalpy, H^{E}, follows the same trends as the G^{E}. H^{E} for mixtures containing saturated hydrocarbons are the largest with 1144 J·mol^{-1} (at $x_1 = 0.5004$) for heptane and 1124 J·mol^{-1} (at $x_1 = 0.4667$) for cyclohexane. The H^{E} value decreases to ca. 637 J·mol^{-1} (at $x_1 = 0.4609$) for 1-hexene. Figure 7 shows the experimental and calculated excess enthalpy as a function of x_1, the mole fraction of propyl ethanoate for the three binary mixtures at $T = 298.15$ K.

The excess functions G^{E} and H^{E} were compared to those predicted by the group contribution method Modified UNIFAC (Dortmund) using the available "ester" main group. The Modified UNIFAC (Dortmund)[25] group contribution method based on the local composition concept has temperature-dependent parameters and needs four parameters per contact (two for Gibbs function and two for enthalpy) to reproduce G^{E} and H^{E}. The equations used to calculate the excess properties are the same as in other applications.[25,26] The group interaction parameters are all available.

The prediction of G^{E} by Modified UNIFAC (Dortmund) is quite satisfactory for the three binary systems. The difference between experimental and calculated G^{E} does not exceed 70 J·mol^{-1}. For H^{E}, the experimental values are (20 to 150) J·mol^{-1} different than those obtained by the Modified UNIFAC (Dortmund) model. The model reproduces fairly well the shapes of both excess functions except for the system (propyl ethanoate + 1-hexene). The comparison between experimental data and Modified UNIFAC (Dortmund) results is presented in a graphical way in Figures 8 to 10.

Summary

VLE data for the three binary mixtures of (propyl ethanoate + heptane), (propyl ethanoate + cyclohexane), or (propyl ethanoate + 1-hexene) were measured at several temperatures using a static device. Deviations from Raoult's law are positive and relatively large. The derived G^{E} data are in good agreement with those predicted by the Modified UNIFAC (Dortmund) group contribution method.

Additionally, excess enthalpies H^{E} were measured for the binary mixtures of propyl ethanoate with heptane, cyclohexane, and 1-hexene at $T = 298.15$ K. The H^{E} data have been compared with data using Modified UNIFAC (Dortmund) and correlated using the Redlich−Kister expansion. Except for the system propyl ethanoate + 1-hexene, the excess enthalpy is at least qualitatively predicted by Modified UNIFAC (Dortmund) using the "ester" main group. This work illustrates the possibility of applying the Modified UNIFAC (Dortmund) group contribution model for the prediction of thermodynamic functions and phase equilibrium of certain polar mixtures involving esters.

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