350 *J. Chem. Eng. Data* **1993,** *38,* 350-352

Vapor Pressures of Binary Mixtures of Hexane + 1-Butanol, + 2-Butanol, + 2-Methyl-1-propanol, or + 2-Methyl-2-propanol at 298.15 K

V. Rodríguez, J. Pardo, M. C. López, F. M. Royo, and J. S. Urieta*

Departamento de Química Orgánica-Química Física, Facultad de Ciencias, Universidad de Zaragoza, Ciudad Universitaria, 50009 Zaragoza, Spain

The total vapor pressures of binary mixtures of hexane + 1-butanol, + 2-butanol, + 2-methyl-1-propanol, or + 2-methyl-2-propanol were measured by a static method at 298.15 K. Vapor-phase compositions, activity coefficients, and excess molar Gibbs energies were calculated by Barker's method.

Introduction

Previous papers (*1–8*) from our laboratory reported measurements of excess enthalpies, excess volumes, vapor pressures, and dipole moments for mixtures containing an alkanol. We have now begun a systematic study of the properties of mixtures containing isomeric butanols. While many studies of the thermodynamic properties of 1-butanol have been published (*9, 10*), only a few systematic investigations have been carried out for mixtures containing isomeric butanols (*11, 12*).

In this work, we have measured the vapor pressures of hexane + each of the butanol isomers at 298.15 K in order to investigate the effect of the position of the OH group in the hydrocarbon chain on the molar excess Gibbs energies, G^E, of the mixtures.

Experimental Section

Materials. The liquids used, namely, 1-butanol, 2-methyl-2-propanol (better than 99.5 mol %), 2-butanol, 2-methyl-1-propanol, and hexane (better than 99 mol %), were obtained from Merck. No further purification was attempted. All the isomers of butanol were dried over activated molecular sieves type 0.3 nm from Merck.

Apparatus. The measurements were carried out using a previously described apparatus (*13, 14*). It consists essentially of a U manometer (25-mm-diameter tube) with unequal arms. The longer arm (about 95 cm), fitted with a reference point, becomes narrower and is connected to the vacuum equipment and, at a certain height, has a small side ampule for introducing the liquids. The whole apparatus was immersed in a water bath equipped with an efficient stirrer. A Beckmann thermometer, previously checked against a calibrated thermistor, was used to measure the temperatures.

In the absence of any systematic error, the main sources of error are (i) the uncertainty of the mole fraction $\sigma(x) = 1 \times 10^{-4}$, (ii) the precision of the cathetometer readings $\sigma(h) = 0.01$ mm, and (iii) the temperature oscillations in the water bath $\sigma(T) = 0.01$ K. The estimated error for each pressure measurement caused by these factors is 0.04%. The standard deviations in the theoretical fitting following Barker's method are less than 1%.

Molar volumes, V, were calculated from densities taken from Timmermans (*15*), and second molar virial coefficients, B_{ii}, of the pure components were obtained using the equation recommended by the Thermodynamics Research Center (*16*). The suitable parameters for this equation are also tabulated in *TRC Tables* (*16*).

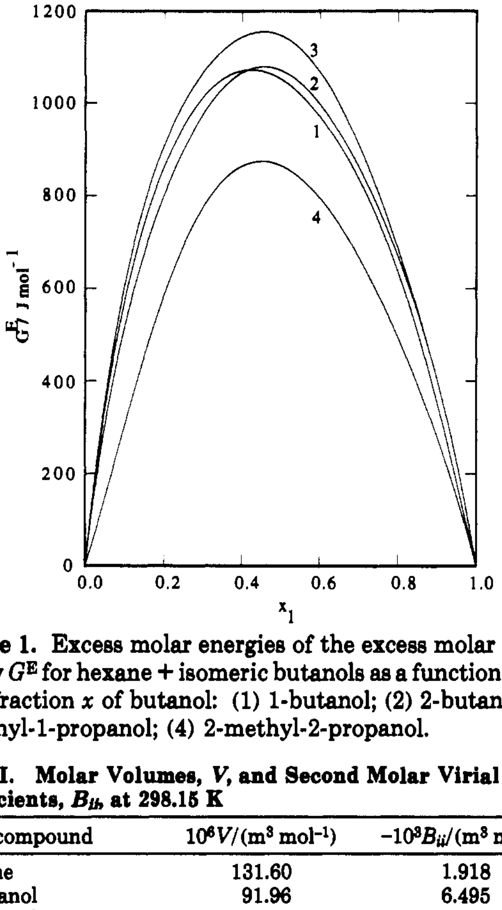

Figure 1. Excess molar energies of the excess molar Gibbs energy G^E for hexane + isomeric butanols as a function of the mole fraction x of butanol: (1) 1-butanol; (2) 2-butanol; (3) 2-methyl-1-propanol; (4) 2-methyl-2-propanol.

Table I. Molar Volumes, *V*, and Second Molar Virial Coefficients, B_{ii}, at 298.15 K

compound	10^6V/(m^3 mol^{-1})	-10^3B_{ii}/(m^3 mol^{-1})
hexane	131.60	1.918
1-butanol	91.96	6.495
2-butanol	92.35	4.474
2-methyl-1-propanol	92.90	5.008
2-methyl-2-propanol	94.87	4.454

Both properties, that is, molar volume and second molar virial coefficients, are used for correcting the nonideality of the vapor phase and are gathered in Table I. Mixed virial coefficients were obtained from the Amdur–Mason equation (*17*):

$$B_{12} = (B_{11}^{1/3} + B_{22}^{1/3})^3/8 \qquad (1)$$

Results and Discussion

On the basis of our vapor-pressure measurements, the composition of vapor, the activity coefficients, and the excess molar Gibbs energies were calculated by Barker's method

0021-9568/93/1738-0350$04.00/0 © 1993 American Chemical Society

Table II. Data for Isomeric Butanols (1) + Hexane (2) Mixtures at 298.15 K: Experimental Liquid-Phase Mole Fraction x_1, and Vapor-Phase Mole Fraction y_1, Total Pressures p, Activity Coefficients γ_1 and γ_2, and Standard Deviations $\sigma(p - p_{calcd})$

x_1	y_1	p/kPa	γ_1	γ_2	x_1	y_1	p/kPa	γ_1	γ_2
				1-Butanol (1) + Hexane (2)					
0.000	0.000	20.174	28.228	1.000	0.637	0.042	15.578	1.205	2.021
0.045	0.020	20.114	10.677	1.021	0.719	0.050	13.542	1.132	2.309
0.153	0.023	20.002	3.470	1.142	0.824	0.065	11.323	1.049	2.992
0.168	0.023	19.798	3.190	1.160	0.878	0.080	9.508	1.019	3.541
0.205	0.024	19.821	2.693	1.206	0.891	0.086	8.631	1.013	3.686
0.226	0.024	19.790	2.488	1.233	0.927	0.115	6.766	1.003	4.068
0.301	0.027	19.345	1.993	1.334	0.961	0.192	4.097	1.000	4.303
0.426	0.030	18.482	1.535	1.546	1.000	1.000	0.823	1.000	4.198
0.471	0.032	17.875	1.432	1.636					
				$\sigma(p - p_{calcd})$/kPa = 0.118					
				2-Butanol (1) + Hexane (2)					
0.000	0.000	20.174	19.300	1.000	0.642	0.115	16.853	1.209	2.069
0.004	0.009	20.220	17.479	1.000	0.718	0.135	15.022	1.148	2.312
0.092	0.056	20.510	4.985	1.057	0.790	0.163	13.327	1.101	2.626
0.148	0.063	20.387	3.437	1.110	0.803	0.169	13.056	1.093	2.695
0.242	0.076	19.867	2.476	1.200	0.839	0.188	11.594	1.070	2.983
0.334	0.086	19.192	1.989	1.310	0.899	0.233	9.901	1.034	3.759
0.394	0.091	19.005	1.747	1.412	1.000	1.000	2.436	1.000	7.566
0.470	0.095	18.646	1.508	1.579					
				$\sigma(p - p_{calcd})$/kPa = 0.116					
				2-Methyl-1-propanol (1) + Hexane (2)					
0.000	0.000	20.174	31.832	1.000	0.655	0.064	17.104	1.189	2.292
0.132	0.039	20.543	4.294	1.124	0.750	0.078	14.857	1.104	2.728
0.141	0.039	20.524	3.995	1.137	0.828	0.102	11.900	1.064	3.128
0.240	0.041	20.187	2.463	1.268	0.872	0.125	10.300	1.045	3.468
0.340	0.048	19.598	1.951	1.393	0.959	0.234	5.659	1.008	5.292
0.499	0.057	18.162	1.478	1.706	1.000	1.000	1.370	1.000	8.035
				$\sigma(p - p_{calcd})$/kPa = 0.113					
				2-Methyl-2-propanol (1) + Hexane (2)					
0.000	0.000	20.174	2.968	1.000	0.570	0.212	18.573	1.206	1.687
0.058	0.059	20.175	3.565	0.996	0.607	0.223	18.240	1.165	1.774
0.109	0.108	20.093	3.471	0.999	0.655	0.242	17.284	1.121	1.892
0.124	0.119	20.086	3.380	1.002	0.696	0.262	16.384	1.093	1.997
0.169	0.145	19.992	3.015	1.022	0.787	0.328	14.389	1.048	2.247
0.230	0.165	19.982	2.499	1.072	0.824	0.367	13.254	1.036	2.364
0.300	0.175	19.873	2.011	1.159	0.850	0.401	12.258	1.027	2.459
0.351	0.179	19.760	1.755	1.238	0.922	0.544	9.600	1.010	2.826
0.396	0.183	19.609	1.579	1.318	0.985	0.840	6.632	1.000	3.468
0.406	0.184	19.604	1.549	1.335	1.000	1.000	5.592	1.000	3.721
0.471	0.192	19.231	1.375	1.465					
				$\sigma(p - p_{calcd})$/kPa = 0.085					

Table III. Coefficients A_i for the Representation of the Excess Molar Gibbs Energy, G^E, at 298.15 by Equation 2

	A_0	A_1	A_2	A_3	A_4	A_5
hexane +						
1-butanol	1.698	−0.417	0.445	0.044	0.244	−0.580
2-butanol	1.729	−0.291	0.121	0.147	0.642	−0.324
2-methyl-1-propanol	1.850	−0.292	0.183	−0.550	0.738	0.154
2-methyl-2-propanol	1.395	−0.299	−0.027	0.225	−0.167	0.187

(*18*) and each set of G^E values was fitted to the smoothing equation

$$G^E/RT = x(1-x)\sum A_i(2x-1)^i \qquad (2)$$

The experimental results of vapor pressure are gathered in Table II, together with the vapor mole fractions, the activity coefficients, and standard deviations σ of $p - p_{calcd}$. The mean deviation of our values for the system hexane + 1-butanol from those of Gracia et al. (*8*) is 0.48 kPa and from those of Smirnova et al. (*19*) is 0.64 kPa. No other directly comparable vapor-pressure data were found by us in the literature although some of these systems have been studied by Maczynska (*20*), Heintz et al. (*21*), Berro (*22*, *23*), Oracz (*24*), and Maciel et al. (*25*) at several temperatures different from 298.15 K. The values of parameters A_i, determined by the least-squares method with all points weighted equally, are gathered in Table III. These results show that $G^E > 0$ and the curves are symmetrical. $G^E(x=0.5)$ increases in the sequence 2-methyl-2-propanol < 1-butanol < 2-butanol < 2-methyl-1-propanol although the values for the mixtures of 1-butanol and 2-butanol are very similar.

G^E values have been calculated by Smirnova et al. (*19*) and by Gracia et al. (*8*) for the system hexane + 1-butanol. They obtained $G^E(x=0.5)$ = 1180 J·mol^{-1} and $G^E(x=0.5)$ = 1082 J·mol^{-1}, respectively. In this work we have obtained $G^E(x=0.5)$ = 1052 J·mol^{-1}, which is in good agreement with the previously mentioned values.

Literature Cited

(1) Pérez, P.; Royo, F.; Gracia, M.; Gutiérrez Losa, C. *J. Chem. Thermodyn.* **1985**, *17*, 711.

(2) Pérez, P.; Gracia, M.; Gutiérrez Losa, C. *J. Chem. Thermodyn.* **1985**, *17*, 1067.

(3) Mateos, M. C.; Pérez, P.; Royo, F.; Gracia, M.; Gutiérrez Losa, C. *Rev. Acad. Cienc. Zaragoza* **1986**, *41*, 73.

(4) Mateos, M. C.; Pérez, P.; Royo, F.; Gracia, M.; Gutiérrez Losa, C. *Rev. Acad. Cienc. Zaragoza* **1986**, *41*, 107.
(5) Iñarrea, J.; Valero, J.; Pérez, P.; Gracia, M.; Gutiérrez Losa, C. *J. Chem. Thermodyn.* **1988**, *20*, 193.
(6) Jiménez, J.; Valero, J.; Gracia, M.; Gutiérrez Losa, C. *J. Chem. Thermodyn.* **1988**, *20*, 931.
(7) Pardo, J.; Rodríguez, V.; López, M. C.; Royo, F. M.; Urieta, J. S. *J. Chem. Thermodyn.* **1992**, *24*, 113.
(8) Gracia, M.; Sánchez, F.; Pérez, P.; Valero, J.; Gutiérrez Losa, C. *J. Chem. Thermodyn.* **1992**, *24*, 463.
(9) Gierycz, P.; Gregorowicz, J.; Malanowski, S. *J. Chem. Thermodyn.* **1988**, *20*, 385.
(10) Stokes, R. H. *J. Chem. Thermodyn.* **1988**, *20*, 1349.
(11) Chaudhari, S. K.; Katti, S. S. *J. Chem. Thermodyn.* **1985**, *17*, 101.
(12) Chao, J. P.; Dai, M. *J. Chem. Thermodyn.* **1991**, *23*, 117.
(13) Mínguez, M.; Chóliz, G.; Gutiérrez Losa, C. *Rev. Acad. Cienc. Exactas, Fis. Nat. Madrid* **1969**, *63*, 533.
(14) Azpiazu, Y.; Royo, F.; Gutiérrez Losa, C. *J. Chem. Thermodyn.* **1984**, *16*, 561.
(15) Timmermans, J. *Physico-Chemical Constants of Pure Organic Compounds*; Elsevier: Amsterdam, 1950.
(16) Selected Values of Properties of Chemical Compounds. *TRC Tables*; Thermodynamic Research Center Data Project: College Station, TX, 1974.
(17) Amdur, I.; Mason, E. A. *Phys. Fluids* **1958**, *1*, 370.
(18) Barker, J. A. *Aust. J. Chem.* **1953**, *6*, 207.
(19) Smirnova, N. A.; Kurtynina, L. M. *Russ. J. Chem.* **1969**, *43*, 1059.
(20) Maczynska, Z. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1983**, 199.
(21) Heintz, A.; Dolch, E.; Lichtentaler, R. N. *Fluid Phase Equilib.* **1986**, *27*, 61.
(22) Berro, C. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1986**, 76.
(23) Berro, C. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1987**, 99.
(24) Oracz, P. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1987**, 236.
(25) Maciel, M. R. W.; Francesconi, A. Z. *Fluid Phase Equilib.* **1989**, *50*, 201.

Received for review April 20, 1992. Revised September 24, 1992. Accepted February 11, 1993. The authors are grateful for financial assistance from the Diputación General de Aragón (Proyecto PCB/90). J.P. especially acknowledges its support (Beca BCB 15/90).