J. Chem. Eng. Data 1980, 25, 159–161

Vapor Pressures and Excess Gibbs Energies in Binary Mixtures of Hydrocarbons at 313.15 K. 1. Methylcyclohexane–Benzene, –Toluene, –*o*-Xylene, –*p*-Xylene, –Ethylbenzene, and –Propylbenzene

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Results of total vapor pressure measurements, performed at 313.15 K by a static method, are reported for six binary mixtures: methylcyclohexane–benzene, –toluene, –*o*-xylene, –*p*-xylene, –ethylbenzene, –propylbenzene. The excess Gibbs energy is expressed with a one-constant equation of the type proposed by Hildebrand and Scatchard by using critical volumes instead of molar volumes. Comparison of the experimental results with the UNIFAC method is also noted.

Introduction

This investigation is part of a research project consisting of the experimental determination of excess Gibbs energies for binary mixtures of selected common solvents at a fixed single temperature. For technical reasons the temperature 313.15 K was chosen. The results are intended to be used for correlations and predictions of g^E for different pairs of substances. A considerable amount of vapor–liquid equilibrium data, determined at 313.15 K for binary systems of the type pyridine base + aliphatic alcohol, have been published recently by Warycha (*6,7*) of this laboratory.

Experimental Section

Methylcyclohexane, benzene, toluene (all A.R. from POCh, Gliwice, Poland), *p*-xylene, ethylbenzene (both Purus, POCh Gliwice), and propylbenzene (Purum Schuhard) were crystallized and then rectified on a column of 80 theoretical plates. Fractions distilling within a 0.01 K (0.02 K for propylbenzene) interval have been collected in each case. The *o*-xylene has been obtained from The Institute of Physical Chemistry of The Polish Academy of Sciences and was used without further purification. The purity of the substances was checked by GLC. Table I gives the results of the purity determination, the measured vapor pressures and their reported values (*1,8*), and the correction terms $B_{ii} - V_i$ and $dB = 2B_{ij} - B_{ii} - B_{jj}$. The second virial coefficients B_{ii} of pure components and B_{ij} for mixtures were calculated according to Pitzer and Curl (*4*). The vapor pressure was measured by a static apparatus described elsewhere (*3*).

Table I. Minimum Mole Fraction of the Main Component x, Vapor Pressure of the Pure Component p, Second Virial Coefficients of Pure Components and Mixtures, B_{ii} and B_{ij}, and Molar Volumes V_i

	10^2x	p/Pa lit.	p/Pa this work	$(B_{ii} - V_i)$/ dm^3 mol^{-1}	$(2B_{ij} - B_{ii} - B_{jj})$/ dm^3 mol^{-1}
methylcyclohexane	99.97	12208	12198	−2.12	
benzene	99.96	24367	24367	−1.34	0.09
toluene	99.91	7886	7886	−2.11	0.00
o-xylene		2046	2056	−2.57	0.02
p-xylene	99.91	2644	2648	−2.54	0.02
ethylbenzene	99.86	2862	2868	−3.05	0.08
propylbenzene	99.91	1103	1115	−4.39	0.41

Table II. Comparison between Three Equations for g^E [a]

MCH–R, R =	σ_1	σ_2	σ_3	V_{c1}/V_{c2}	T_{c1}/T_{c2}
benzene	130	17	15	1.42	0.98
toluene	18	12	8	1.17	1.03
o-xylene	33	40	32	1.04	1.10
p-xylene	35	38	35	1.04	1.08
ethylbenzene	23	25	22	1.04	1.08
propylbenzene	24	20	17	0.84	1.12

[a] Standard errors of vapor pressure resulting from applying eq 1, 2, and 3 are σ_1, σ_2, σ_3 respectively, the molar critical volume is V_c, and the critical temperature is T_c. Standard errors of pressure are given in pascals.

Results and Discussion

At first the excess of Gibbs energy was approximated by two single-constant equations.

$$g^E/RT = x(1 - x)A \tag{1}$$

$$g^E/RTV = z(1 - z)B \tag{2}$$

Equation 1 is obviously the Redlich–Kister equation with one adjustable constant, A. The second equation was proposed by Hildebrand and Scatchard, but in our work the parameter B is an adjustable one. In this equation z denotes volume fraction and V is the molar volume of the ideal mixture; i.e., $V = x_1V_1 + x_2V_2$. The second equation gives significantly better results for the systems methylcyclohexane (MCH)–benzene and MCH–toluene. In other investigated systems the difference between molar volume of MCH and the second component is relatively small, whereas differences between the critical temperatures of the two constituent components of the mixture are much greater; i.e., the two components are in different degrees of expansion and molar volume is not a good measure of the volume of a single molecule. It is possible that these two factors cause eq 1 to give a somewhat better approximation for MCH with *o*-xylene, *p*-xylene, and propylbenzene. For these reasons a third equation has been tried, where critical volumes have been used instead of molar volumes. The idea of using such an equation is due to van Laar

$$g^E/RTV_c = Z(1 - Z)C \tag{3}$$

where V_{c1}, V_{c2} are critical volumes, $V_c = x_1V_{c1} + x_2V_{c2}$ and $Z = x_1V_{c1}/V_c$. Equation 3 with one adjustable parameter C gives the best results and has been chosen to express the excess Gibbs energy in this paper. A comparison of these three equations is shown in Table II. The total vapor pressure p, liquid-phase composition x, and calculated vapor-pressure mole fraction y are given in Table III. In Table IV, values of parameter C in eq 3 and its standard errors are presented together with the critical volumes used in eq 3. They were used in

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0021-9568/80/1725-0159$01.00/0

Table III. Liquid-Phase Mole Fraction x, Calculated Vapor-Phase Mole Fraction y, and Vapor Pressure p

x	y	p/hPa	x	y	p/hPa	x	y	p/hPa
			x Benzene-$(1-x)$ Methylcyclohexane					
0	0	121.98	0.3974	0.5966	193.70	0.7497	0.8272	229.54
0.0572	0.1470	135.24	0.4468	0.6349	200.01	0.7923	0.8530	232.57
0.0962	0.2278	143.48	0.5027	0.6747	206.60	0.8398	0.8826	236.02
0.1586	0.3343	155.77	0.5323	0.6945	210.05	0.8891	0.9151	238.91
0.1922	0.3828	162.11	0.5908	0.7319	216.14	0.9385	0.9503	241.31
0.2422	0.4460	170.76	0.6376	0.7605	220.02	1	1	243.66
0.3440	0.5508	186.38	0.6937	0.7940	225.15			
			x Toluene-$(1-x)$ Methylcyclohexane					
0	0	121.98	0.4064	0.3241	113.11	0.7541	0.6242	97.67
0.0492	0.0438	121.40	0.4590	0.3642	111.35	0.7700	0.6417	96.85
0.1492	0.1272	119.80	0.5020	0.3976	109.79	0.8631	0.7578	90.62
0.1975	0.1655	118.79	0.5420	0.4295	108.11	0.8997	0.8119	87.86
0.2476	0.2042	117.52	0.5848	0.4647	106.40	0.9524	0.9020	83.55
0.2918	0.2379	116.39	0.6453	0.5174	103.51	1	1	78.86
0.3548	0.2852	114.70	0.6932	0.5621	101.20			
			x o-Xylene-$(1-x)$ Methylcyclohexane					
0	0	121.98	0.3073	0.0787	95.33	0.6941	0.2500	58.80
0.0403	0.0101	118.31	0.4551	0.1258	82.11	0.7475	0.2963	52.68
0.1004	0.0250	113.24	0.4991	0.1426	78.11	0.7917	0.3450	48.04
0.1502	0.0374	109.06	0.5441	0.1619	74.17	0.8375	0.4104	42.62
0.2062	0.0515	103.99	0.6012	0.1902	68.47	1	1	20.56
0.2552	0.0644	99.82	0.6524	0.2206	63.03			
			x p-Xylene-$(1-x)$ Methylcyclohexane					
0	0	121.98	0.3470	0.1115	93.45	0.7384	0.3487	57.26
0.0514	0.0156	117.66	0.4046	0.1341	88.19	0.7957	0.4180	50.92
0.0982	0.0298	113.99	0.4502	0.1536	84.33	0.8341	0.4767	46.84
0.1463	0.0445	110.04	0.4879	0.1712	81.01	0.8885	0.5848	40.56
0.1988	0.0609	105.87	0.5614	0.2102	74.34	0.9503	0.7670	33.17
0.2483	0.0769	101.66	0.6462	0.2663	66.35	1	1	26.48
0.2933	0.0922	97.85	0.6935	0.3049	61.78			
			x Ethylbenzene-$(1-x)$ Methylcyclohexane					
0	0	121.98	0.4053	0.1458	89.13	0.8091	0.4538	51.64
0.0541	0.0177	117.76	0.4505	0.1664	85.51	0.8785	0.5765	43.96
0.0880	0.0289	115.10	0.5673	0.2290	75.33	0.8994	0.6243	41.85
0.1508	0.0498	109.98	0.5998	0.2498	72.41	0.9581	0.8044	34.66
0.2044	0.0683	105.70	0.6410	0.2789	68.74	1	1	28.68
0.2520	0.0852	101.90	0.6958	0.3241	63.49			
0.3004	0.1031	97.94	0.7466	0.3747	58.41			
			x Propylbenzene-$(1-x)$ Methylcyclohexane					
0	0	121.98	0.3522	0.0513	86.19	0.7106	0.1682	48.32
0.0785	0.0099	113.63	0.3958	0.0598	81.83	0.7590	0.2022	42.65
0.1232	0.0158	109.71	0.4409	0.0695	77.19	0.8160	0.2578	35.77
0.1712	0.0224	104.30	0.4939	0.0824	71.66	0.8744	0.3467	28.28
0.2090	0.0278	100.55	0.5471	0.0975	66.21	0.9330	0.5084	20.70
0.2551	0.0348	95.87	0.5946	0.1135	61.13	1	1	11.15
0.3076	0.0434	90.66	0.6461	0.1343	55.49			

Table IV. Dimensionless Critical Volumes Used in Equation 3 V_c, Adjustable Parameter C with Its Standard Deviation σ, Equimolar Value of Excess Gibbs Energy $g^E{}_{0.5}$ with Its Standard Deviation σ_g, and Difference Δ between Experimental Value of $g^E{}_{0.5}$ and Its Value Calculated by the UNIFAC Method

	V_c	$10^3(C \mp \sigma)$	$g^E{}_{0.5} \mp \sigma_g$/ J mol^{-1}	Δ/J mol^{-1}
methylcyclohexane	0.995			
-benzene	0.700	553 ∓ 1	296 ∓ 0.5	38
-toluene	0.854	393 ∓ 1	235 ∓ 0.5	12
-o-xylene	0.997	365 ∓ 5	237 ∓ 3.2	68
-p-xylene	1.024	298 ∓ 5	196 ∓ 3.2	27
-ethylbenzene	1.011	310 ∓ 3	202 ∓ 2.2	21
-propylbenzene	1.189	243 ∓ 3	171 ∓ 1.8	51

dimensionless reduced form $V_{ci} = V_{ci}/V_{c0}$, where V_{c0} is the critical volume of hexane (V_{c0} = 370 cm^3). Table IV also gives a comparison between experimental values of g^E and values calculated by the UNIFAC method. The results obtained by the UNIFAC method agree relatively well with experiment. Although the substances investigated here are common solvents there

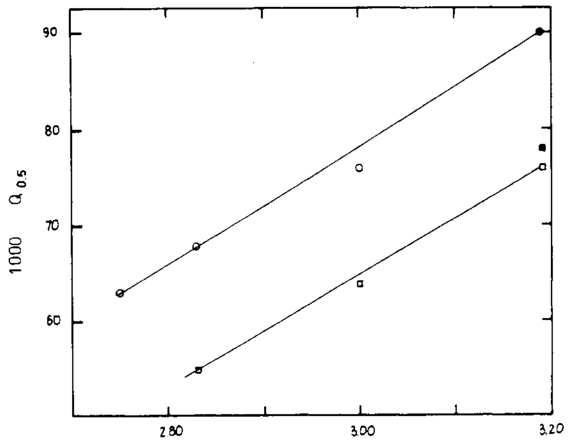

Figure 1. Comparison of the equimolar value of $Q = g^E/RT$ with literature data: toluene-methylcyclohexane, (○) Schneider (*5*), (●) our result; ethylenebenzene-methylcyclohexane, (□) Funk et al. (*2*), (■) our result.

are only a few vapor–liquid (VLE) data for the systems MCH + toluene and MCH + ethylbenzene. The VLE data for MCH + benzene consist of isothermic measurements. There is a complete lack of (either isobaric or isothermal) VLE data for MCH + *o*-xylene, MCH + *p*-xylene, and MCH + propylbenzene. A direct comparison of our results can be made with data of Funk et al. (*2*) for the MCH + ethylbenzene system and less directly, because of differences in temperature, with the data of Schneider (*5*) for the MCH + toluene system. To give a comparison with data obtained at different temperatures, we plotted $Q_{0.5}$, the equimolar value of g^E/RT vs. $1/T$ in Figure 1, giving a straight line in the temperature interval considered. The slope of this line for the MCH + toluene system gives $H^E{}_{0.5} = 507$ J. This average value in the 313–363 K interval agrees well with the data of Wôjcicki (*9*), who obtained $H^E{}_{0.5} = 523$ J at a temperature of 298 K. For the second system the difference between our results and the data of Funk et al. (*2*) is about 5 J. It is evident from Figure 1 that such a difference lies within the limits of experimental error.

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Received for review August 16, 1979. Accepted January 10, 1980. This work was supported by the Polish Academy of Sciences within the project PAN 03.10.

Ammonium Iodide–Potassium Iodide Mixed Crystals in Equilibrium with Aqueous and Aqueous–2-Propanol Solutions

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The equilibria in the systems KI + HN_4I + water and KI + HN_4I + equimolar mixtures of 2-propanol and water have been studied at 25 °C. The two iodides are completely miscible in the solid phase.

Introduction

In a recently proposed cycle for the thermochemical production of hydrogen (*1*, *2*), the water-binding step is the reaction

$$KI + H_2O + NH_3 + CO_2 \rightarrow KHCO_3 + NH_4I$$

This reaction is carried out in an equimolar mixture of water and 2-propanol, potassium bicarbonate precipitates, and the supernatant solution contains a mixture of KI and NH_4I from which the latter must be separated. The present investigation has been undertaken to elucidate the phase behavior of solid KI and NH_4I in equilibrium with such solutions, as well as with purely aqueous solutions of the two salts. We hoped to find a means of precipitating NH_4I from the solutions that would be analogous to the method employed to recover NH_4Cl in the modified Solvay process (*3*).

A study of the NH_4Cl–KCl–H_2O and NH_4Br–KBr–H_2O systems has been reported (*4*). In both of these cases the potassium and ammonium salts exhibit limited mutual solubility. No comparable investigation of the iodide system appears to have been carried out.

Experimental Section

Analytical reagent grade chemicals were used without further purification.

Due to the limited mobility of ions within a solid and the different ratios of K^+/NH_4^+ in the solid and solvent phases, establishment of equilibrium on mixing solid and solvent may be slow. Therefore equilibrium was approached by precipitation of solid from a solvent phase whose composition varied little during the experiment.

Experiments with Equimolar Water–2-Propanol Solutions. Two burets were used to deliver simultaneously over 10 s 3 mL of 2-propanol and about 1.1 mL of aqueous KI–NH_4I solution to a stirred flask thermostated at 25 °C. Volumes were such as to produce a final water/2-propanol mole ratio of 1:1. Precipitation of NH_4I–KI occurred due to reduced solubility in the mixed solvent. The solution and solid were allowed to equilibrate for 30–60 s before the cycle was repeated. Since momentary deviations from equimolar 2-propanol–water on addition and mixing, with resultant inhomogeneity of the solid, are more likely when the solution volume is small, the solid was discarded after addition of the first 24 mL of 2-propanol. Cycles of simultaneous aliquot addition to the retained solution followed by equilibration were continued until sufficient precipitate had collected. The resulting mixture was stirred for 20–24 h, the solution was decanted, the solid was dried, and both phases were analyzed for NH_4^+, K^+, and I^-. The solvent mass loss on drying of the solid was used in conjunction with the density and composition of the mother liquor to correct the composition of the solid for deposition of salts from adhering mother liquor.

Experiments with Aqueous Solutions. A stream of nitrogen was introduced over the surface of a stirred saturated aqueous solution of NH_4I + KI at 25 °C to induce evaporation of water and precipitation. Since solid that formed on the sides of the flask through evaporation would tend to have the composition of evaporated solution, care was taken to avoid contamination of the equilibrium solid phase distributed throughout the liquid with this solid. After the desired amount of precipitate was obtained, the nitrogen stream was stopped, the flask stoppered, and the mixture stirred for 3–20 h. One aliquot of liquid was removed for analysis on initiation of precipitation, and another was taken after the equilibration period. The results were averaged. Since the precipitated solid contained a higher pro-

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