(4) Modell, M.; deFillippi, R. P.; Krukonis, V. J. "Regeneration of Activated Carbon with Supercritical Carbon Dioxide", presented at the National Meeting of the American Chemical Society, Miami, FL, Sept 14, 1978.
(5) Gouw, T. H.; Jentoft, R. E. *J. Chromatogr.* **1972**, *68*, 303.
(6) Francis, A. W. *J. Phys. Chem.* **1954**, *58*, 1099.
(7) Tsekhanskaya, Y. V.; Iomtev, M. B.; Muskina, E. V. *Russ. J. Phys. Chem.* (*Engl. Transl.*) **1964**, *38*, 1173.
(8) Rowlinson, J. S. "Liquids and Liquid Mixtures"; Butterworth: London, 1969; pp 202–21.
(9) Diepen, G. A. M.; Scheffer, F. E. C. *J. Phys. Chem.* **1953**, *57*, 575.
(10) Mackay, M. E.; Paulaitis, M. E. *Ind. Eng. Chem. Fundam.* **1979**, *18*, 149.
(11) Büchner, E. H. *Z. Phys. Chem., Stoechiom. Verwandschaftsl.* **1906**, *54*, 665.
(12) von Tapavicza, S.; Prausnitz, J. M. *Int. Chem. Eng.* **1976**, *16*, 329.

Received for review January 19, 1980. Accepted June 30, 1980. The authors gratefully acknowledge the financial support provided for a portion of this work by the National Science Foundation under Grant No. ENG78-05584.

Vapor–Liquid Equilibria for the System *n*-Heptane–*o*-Xylene at 348.1, 358.1, and 368.3 K

Patricio C. Proust,* Alberto L. Ramirez, and Juan B. Ylanatos
School of Chemical Engineering, Universidad Catolica de Valparaiso, Casilla 4059, Valparaiso, Chile

Isothermal vapor–liquid equilibrium data for the *n*-heptane–*o*-xylene system have been determined at 348.1, 358.1, and 368.3 K in a modified Fowler–Norris cell. The data have been correlated by using Barker's method together with the four-suffix Margules equation.

Introduction

A survey of the vapor–liquid equilibrium data compilation by Wichterle et al. (*8*), and of the more recent literature, revealed that the *n*-heptane–*o*-xylene system has not been investigated. Wichterle (*7*) and Michishita et al. (*5*) report data for the *n*-heptane–*p*-xylene system at 90 °C and 760 mmHg, respectively.

Mixtures of paraffinic and aromatic hydrocarbons are important from a theoretical and a practical viewpoint. Accordingly, the equilibrium pressures and phase compositions for the *n*-heptane–*o*-xylene system were measured under isothermal conditions of 348.1, 358.1, and 368.3 K.

Experimental Section

The reagents used were manufactured by Hopkin & Williams, Ltd. (England), and were AnalaR (pro-analysi) grade. They were further purified by distillation in a 20-plate Oldershaw column, operated at a high reflux rate, and from which heart cuts were collected. The physical properties of the two components, together with the corresponding literature values, are listed in Table I.

The equilibrium apparatus was a modified Fowler–Norris cell (*3*), in which both phases are recirculated. It is described by Kesselman et al. (*4*). The two Teflon sampling plugs had a narrow perforation covered by a rubber septum held in place by a special brass screw. Samples were withdrawn with hypodermic syringes after puncturing the septum.

The cell was connected to a constant-pressure system consisting of a cartesian manostat, a mercury manometer, which could be read to within ±0.013 kPa (0.1 mmHg), a 5 × 10^{-3} m^3 ballast flask, a vacuum pump, and a regulated supply of dry air.

The equilibrium temperature was measured to within ±0.1 K with certified mercury thermometers.

Composition of the coexisting phases was determined by measuring the refractive index at 25 °C. Previously, this property was measured for mixtures of known composition and was correlated, within experimental uncertainty, by the equation

$$n_D(x_1) = 1.3850x_1 + 1.5025x_2 - \frac{x_1x_2}{50.8397 - 14.6474x_1} \qquad (1)$$

Table I. Physical Properties of the Pure Components

	n-heptane		*o*-xylene	
	exptl	lit.[a]	exptl	lit.[a]
density, g/cm³ (20 °C)	0.6839	0.68376	0.8800	0.88020
refractive index (25 °C)	1.3850	1.38511	1.5025	1.50295
vapor pressure, kPa				
348.1 K	47.96	48.02	10.22	10.31
358.1 K	66.93	66.90	15.30	15.30
368.3 K	91.98	91.81	22.19	22.29

[a] Reference 1.

The refractive index was read to within ±0.0001 units.

The estimated experimental uncertainties are as follows: temperature ±0.1 K; pressure ±0.067 kPa; composition ±0.005 mole fraction.

Results

Experimental temperatures, pressures, and liquid- and vapor-phase mole fractions of *n*-heptane are reported in Table II and shown graphically in Figure 1.

Correlation of the Data and Discussion

In order to smooth the experimental data and get an indirect check of their thermodynamic consistency, we used the method proposed by Barker (*2*). On the assumption that the excess Gibbs free energy of the mixture was represented by the four-suffix Margules equation

$$g = G^E/RT = x_1x_2(A_{21}x_1 + A_{12}x_2 - Dx_1x_2) \qquad (2)$$

equilibrium pressures were calculated as

$$P = \frac{x_1\varphi_1{}^sP_1{}^s}{\varphi_1}\exp\left[\frac{v_1{}^L}{RT}(P - P_1{}^s)\right]\exp\left(g + x_2\frac{dg}{dx_1}\right) + \frac{x_2\varphi_2{}^sP_2{}^s}{\varphi_2}\exp\left[\frac{v_2{}^L}{RT}(P - P_2{}^s)\right]\exp\left(g - x_1\frac{dg}{dx_1}\right) \qquad (3)$$

The vapor pressures were the experimental values.

Vapor-phase fugacity coefficients φ_i and $\varphi_i{}^s$ were calculated from the virial equation of state, truncated after the second virial coefficient. Pure-component and interaction second virial coefficients were obtained from the generalized correlation of Tsonopoulos (*6*). Liquid volumes were taken from ref 1. All these quantities are listed in Table III.

Using a nonlinear least-squares regression scheme, which minimized the deviations between calculated and experimental

0021-9568/80/1725-0329$01.00/0

Table II. Experimental and Calculated Vapor-Liquid Equilibrium Data for the System *n*-Heptane-*o*-Xylene

exptl			calcd values at exptl *x*'s			
x_1	P, kPa	y_1	P, kPa	y_1	γ_1	γ_2
			348.1 K			
0.0	10.22	0.0	10.22	0.0	1.551	1.000
0.008	10.63	0.051	10.68	0.051	1.538	1.000
0.033	12.16	0.193	12.21	0.189	1.495	1.001
0.075	14.53	0.348	14.55	0.346	1.431	1.003
0.152	18.40	0.516	18.35	0.519	1.333	1.012
0.238	22.04	0.629	22.06	0.633	1.247	1.029
0.364	26.89	0.739	26.86	0.739	1.153	1.064
0.485	30.97	0.809	31.00	0.808	1.091	1.107
0.623	35.50	0.865	35.54	0.870	1.044	1.169
0.730	39.04	0.906	39.00	0.911	1.021	1.225
0.872	43.66	0.958	43.64	0.959	1.004	1.309
1.0	47.96	1.0	47.96	1.0	1.000	1.397
			358.1 K			
0.0	15.30	0.0	15.30	0.0	1.497	1.000
0.007	15.77	0.040	15.84	0.040	1.488	1.000
0.082	21.58	0.346	21.57	0.343	1.389	1.003
0.153	26.27	0.497	26.28	0.497	1.312	1.011
0.227	30.74	0.601	30.75	0.602	1.243	1.024
0.365	38.05	0.725	38.00	0.724	1.147	1.059
0.495	44.06	0.798	44.10	0.802	1.084	1.105
0.605	49.04	0.854	49.06	0.854	1.047	1.152
0.735	54.84	0.905	54.81	0.907	1.019	1.217
0.861	60.54	0.954	60.50	0.953	1.005	1.287
1.0	66.93	1.0	66.93	1.0	1.000	1.367
			368.3 K			
0.0	22.19	0.0	22.19	0.0	1.404	1.000
0.048	27.01	0.219	27.06	0.216	1.375	1.001
0.083	30.52	0.328	30.46	0.327	1.352	1.002
0.150	36.62	0.472	36.61	0.476	1.304	1.006
0.227	42.97	0.584	43.02	0.589	1.249	1.017
0.372	53.56	0.719	53.52	0.720	1.152	1.053
0.493	61.26	0.793	61.24	0.792	1.088	1.100
0.598	67.31	0.842	67.35	0.843	1.047	1.151
0.731	75.19	0.899	75.19	0.899	1.015	1.222
0.862	83.17	0.950	83.14	0.951	1.002	1.284
1.0	91.98	1.0	91.98	1.0	1.000	1.313

Table III. Second Virial Coefficients and Liquid Volumes[a]

T, K	B_{11}	B_{22}	B_{12}	v_1^L	v_2^L
348.1	−1827	−2478	−2091	157.7	127.3
358.1	−1680	−2245	−1912	160.1	128.7
368.3	−1550	−2044	−1754	162.7	130.1

[a] B's and v^L's in cm³/mol.

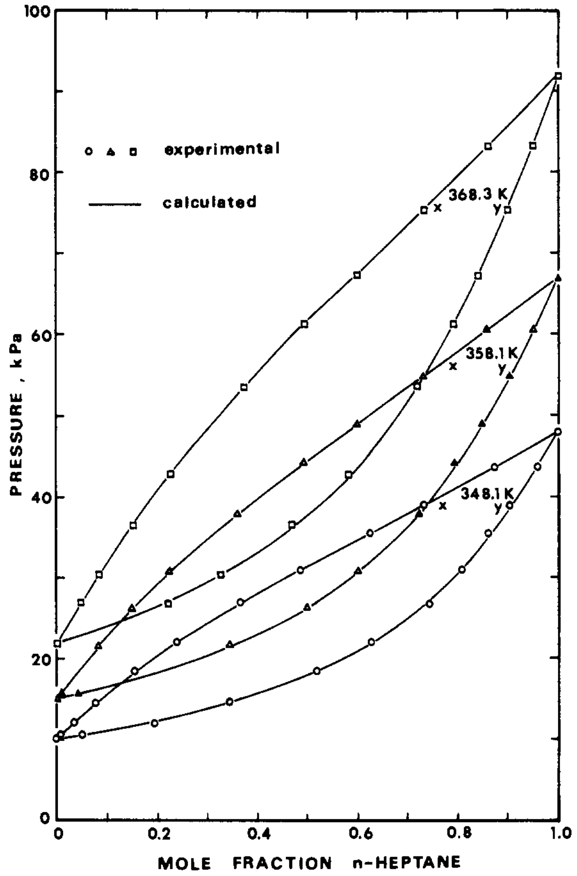

Figure 1. P-x-y data for the *n*-heptane-*o*-xylene system at 348.1, 358.1, and 368.3 K.

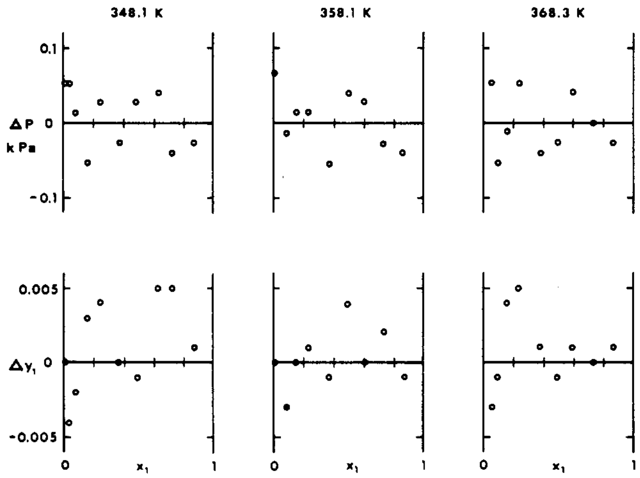

Figure 2. Differences between calculated and experimental pressures and vapor mole fractions of *n*-heptane.

Table IV. Constants of the Margules Equation

T, K	A_{12}	A_{21}	D
348.1	0.4392	0.3344	0.03213
358.1	0.4036	0.3128	−0.009221
368.3	0.3391	0.2724	−0.2093

pressures, values of the three Margules parameters were calculated for each isotherm.

Vapor-phase mole fractions y_1 and y_2 obtained from eq 3 can then be compared with the experimental values.

The calculated pressures, vapor mole fractions y_1, and activity coefficients of both components are included in Table II. The first two quantities are also plotted in Figure 1. The parameters of the Margules equation are listed in Table IV.

Differences between calculated and experimental pressures and vapor mole fractions of *n*-heptane are shown in Figure 2. Absolute maximum, root-mean-squared, and bias values of these differences are reported in Table V.

It is observed that the individual values of ΔP and Δy_1 are within the range of experimental uncertainty. There is a slight overall positive bias for Δy_1. It can be concluded that the data reported here are thermodynamically consistent.

Glossary

A_{12}, A_{21}, D	parameters of the Margules equation
B	second virial coefficient, cm³/mol
G^E	excess Gibbs free energy, J/mol
n_D	refractive index
P	pressure, kPa
P^s	vapor pressure, kPa
T	temperature, K
v^L	liquid volume, cm³/mol
x	liquid-phase mole fraction
y	vapor-phase mole fraction
γ	activity coefficient

Table V. Results of Data Reduction[a]

	348.1 K	358.1 K	368.3 K
abs max ΔP, kPa	0.053	0.067	0.053
RMS ΔP, kPa	0.039	0.037	0.038
ΔP bias, kPa	+0.0067	+0.0030	−0.0015
abs max Δy_1	0.005	0.004	0.005
RMS Δy_1	0.0031	0.0019	0.0025
Δy_1 bias	+0.0011	+0.0002	+0.0008

[a] Δ = calculated value − experimental value.

φ_i, φ_i^s fugacity coefficient of component i in the vapor mixture and as pure, saturated vapor

Subscripts

1 *n*-heptane
2 *o*-xylene

Literature Cited

(1) American Petroleum Institute Research Project 44, "Selected Values of Properties of Hydrocarbons and Related Compounds", Thermodynamics Research Center, Texas A&M University, College Station, Texas (10/31/1970).
(2) Barker, J. A., *Aust. J. Chem.*, **6**, 207 (1953).
(3) Hála, E., Pick, J. Fried, V., Vilim, O., "Vapour-Liquid Equilibrium", Pergamon Press, New York, 1958, p 272.
(4) Kesselman, W. D., Hollembach, G. E., Myers, A. L., Humphrey, A. E., *J. Chem. Eng. Data*, **13**, 34 (1968).
(5) Michishita, T., Arai, Y., Saito, S., *Kagaku Kogaku*, **35**, 111 (1971).
(6) Tsonopoulos, C., *AIChE J.*, **20**, 263 (1974).
(7) Wichterle, I., *Collect Czech. Chem. Commun.*, **30**, 3388 (1965).
(8) Wichterle, I., Linek, J. Hála, E. "Vapour-Liquid Equilibrium Data Bibliography", American Elsevier, New York, 1973, Supplement 1, 1975.

Received for review February 1, 1980. Accepted May 19, 1980.

Vapor Pressures of Aqueous Solutions of $(Ag,Tl,Na)NO_3$ at 98.5 °C

Marie-Christine Abraham and Maurice Abraham
Département de Chimie, Université de Montréal, C.P. 6210, Succursale "A", Montréal, Québec, Canada H3C 3V1

James Sangster*
Département de Génie Chimique, Ecole Polytechnique, Campus de l'Université de Montréal, C.P. 6079, Succursale "A", Montréal, Québec, Canada H3C 3A7

Vapor pressures of aqueous solutions of the liquid melt $(Ag,Tl,Na)NO_3$ at 98.5 °C and Ag/Tl = 1.06 have been measured in the water-poor region by the static technique. The mole fraction of $NaNO_3$ in the melt was 0.025, 0.050, 0.075, and 0.101. The data was fitted to a form of the BET equation adapted to concentrated aqueous solutions, and BET parameters were deduced. These allowed the calculation of Henry's constant for water dissolved in the melt, and, by use of a simple previously verified additivity rule, parameters for the pure third salt ($NaNO_3$) were extracted.

Introduction

There are relatively few thermodynamic data for electrolyte solutions in the water-poor region of concentration. Solubility limits contribute to this lack. These data however are needed for suggesting and testing theories of concentrated electrolyte solutions, of which there are few which are successful. Not long ago we measured the vapor pressures of the system $(Ag,Tl)NO_3$ + H_2O, which is liquid over the complete water concentration range below 100 °C (*1a*). Later we studied the systems $(Ag,Tl,M)NO_3$ + H_2O at the same temperature, where M = Cd (*1b,c*), Ca (*1d*), or Cs (*1e*). In all cases the water activity data could be represented by a modified BET equation, and the BET constants varied linearly with the third cation concentration in the melt. Henry's constants for water dissolved in molten salt were also deduced.

In the present paper we report vapor pressure data for aqueous solutions of $(Ag,Tl,Na)NO_3$ under experimental conditions uniform with our previous work.

Experimental Section

Vapor pressures were measured by the static method, the details of which were given previously (*1a*). The preparation of the salt mixture has also been given (*1e*). The Ag/Tl ratio was fixed at 1.06, and $NaNO_3$ (Anachemia Reagent, used without further purification) was added to the melt to give $NaNO_3$ melt mole percentages of 2.5, 5.0, 7.5, and 10.1, indicated by $S_{2.5}$, S_5, $S_{7.5}$, and $S_{10.1}$ (*1b*). S_0 represents the system with no $NaNO_3$ added.

The data were treated as before (*1a*), the fugacity f of water being calculated from the pressure p by means of the second virial coefficient at 98.5 °C; the water activity is then $a_w = f/f_0$, where f_0 is the fugacity of pure water at the temperature in question. Water activity and mole fraction x_w in the solution are related to the water activity coefficient γ_w by $a_w = x_w\gamma_w$.

Results and Discussion

The data for the four systems $S_{2.5}$–$S_{10.1}$ are given in Table I as x_w, p, f, a_w, and γ_w. As before, the data can be represented satisfactorily by an adapted BET adsorption isotherm (*2*) in the form

$$a_w(1 - x_w)/x_w(1 - a_w) = 1/cr + (c - 1)a_w/cr \qquad (1)$$

where c and r are the BET constants. In this model water is considered to occupy sites provided by the molten salt. The mole ratio of adsorption sites to salt is r, and c is the Boltzmann factor $\exp(-\Delta E/RT)$, where $\Delta E = E_{ads} - E_L$ is the difference between the energy of adsorption of water by a bare site and the energy of condensation of water into pure water (or onto a sorbed water molecule).

The data plotted according to eq 1 appear in Figure 1; the coefficients of correlation for these straight lines are respectively 0.9998, 0.9994, 0.9986, and 0.9992 for $S_{2.5}$, S_5, $S_{7.5}$, and $S_{10.1}$. As indicated previously (*1a*, *3*), the BET intercept $1/cr = \gamma_w^\infty$, the activity coefficient of water at infinite dilution in molten salt; from this can be calculated Henry's law constants K_H through eq 2. The BET parameters and derived quantities for the

$$f = f_0\gamma_w^\infty x_w = K_H x_w \qquad (2)$$

0021-9568/80/1725-0331$01.00/0