Measurement of Excess Enthalpies with Tronac Titration Calorimeter. Data for Some C$_8$ Aromatic Binaries

Don L. Holt and Buford D. Smith[1]
Thermodynamics Research Laboratory, Washington University, Box 1144, St. Louis, Mo. 63130

The operation of a new Tronac calorimeter with an open reaction vessel is described. The accuracy of the instrument for nonvolatile systems is established by an acid-base titration. A process model is developed for the interaction between the liquid and vapor phases but proves inadequate for heat of mixing measurements on systems more volatile than benzene–cyclohexane at 35°C. Data measured for isomeric xylene binaries at 25°C agree well with the measurements of Lam et al. New data are presented for C$_8$ aromatic binaries at 25° and 70°C.

A Tronac titration calorimeter has been applied to the measurement of excess enthalpies (heat of mixing) for liquid mixtures. The prototype model of this instrument was developed by Christensen and Izatt at Brigham Young; refer to the work of Christensen et al. (1) for a description of the prototype models. The instrument was further developed (particularly in the electronic auxiliaries) by Tronac, Inc., and is now marketed by that organization. Details of the commercially produced model are available from the manufacturer (Tronac, Inc., 1804 S. Columbia Lane, Orem, Utah 84601).

The instrument can operate in either the adiabatic or isothermal mode. It is highly automated and prints out the data in digital form. A titration run (half of the H^E curve) usually takes 25–30 min, and the titration can be performed continuously or by pulsed injections. The calorimeter can cover the temperature range from 0° to 80°C and can cover the entire range of energy effects encountered in heat of mixing work with nonelectrolyte liquid mixtures. Its use in the lower end of that range is demonstrated by the C$_8$ aromatic binary data presented in this paper.

The calorimeter was originally developed for the measurement of heats of reaction in aqueous solutions. Such work can be done safely in an open reaction vessel (one with a vapor space vented to the atmosphere) because of the low volatility of water at the temperatures of interest (usually 25°C). Consequently, when the calorimeter was purchased, only an open reaction vessel was available for immediate use. Unfortunately, the development of the needed closed vessel (no vapor space) has been delayed, and in order to use the instrument until the closed vessel could be installed, it was necessary to first determine the volatility limits for liquid systems which can be measured accurately in an open reaction vessel. This was done by first establishing the accuracy of the instrument by measuring the heat of ionization of water at 25°C where the vapor space was not an important factor. Then the effect of the vapor space was checked with the cyclohexane–n-hexane system at 25°C and the benzene–cyclohexane system at 35°C. An important error was incurred in the former, but with the latter system, the results duplicated literature data obtained with a closed vessel. Hence, it was concluded that the vapor space could be modeled with sufficient accuracy to handle sys-

tems with volatilities less than that of the benzene–cyclohexane system at 35°C. The study of the C$_8$ aromatic systems was then begun to establish the capability of the instrument for systems with small H^E values.

All of the hydrocarbons used in the experimental measurements were obtained from the Special Products Division, Phillips Petroleum Co., Bartlesville, Okla. The minimum purity specifications and the typical purities (in parentheses) in mole percents were as follows: cyclohexane, 99.5 (99.8); n-hexane, 99.0 (99.3); benzene, 99.0 (99.84); p-xylene, 99.0 (99.3); m-xylene, 99.0 (99.3); o-xylene, 99.0 (99.2); and ethylbenzene, 99.0 (99.2). Other properties are listed in the Phillips Petroleum catalog available upon request.

Calibration

The calorimeter electronics are periodically calibrated by use of a standard resistor and a constant voltage power supply. The standard Leeds and Northrup resistor has a resistance of 100.0001 ohms ± 0.001%. In the initial calibration procedure, the voltage applied to the terminals of the resistor is adjusted to a value of 10.000 V. The calibration heater in the reaction vessel also has a resistance of about 100 ohms. When the calibration heater is switched into the circuit in place of the standard resistor, the current to the heater and its voltage drop are determined through a network of resistive dividers. The values of current and voltage are then electronically manipulated so that their product gives the energy dissipated in the heater in units of millicalorie/second (cal = 4.184 J).

In a calibration run the calibration heater is operated in place of the titration buret. The energy that is actually dissipated during this thermal event is compared to the value measured by the calorimeter. The ratio of these two values produces a calibration factor that is applied to the data from the experimental runs. The product of the measured heat effect and the calibration factor gives the true heat effect that took place in the reaction vessel.

During the work reported here, this calibration procedure was repeated automatically several times in overnight runs before each titration run. The calibration factors from the repeated runs were averaged, and the average calibration factor was used in the calculations.

Process Model

Energy and mass balances. The various terms involved in the energy and mass balances around the liquid phase in the reaction vessel are shown in Figure 1. Certain terms (the potential and kinetic energies of the three mass streams and the change in the kinetic energy of the system mass) are negligible and can be dropped from the balance which reduces to the following form when the reference states are defined as the pure liquids at the temperature and pressure of the systems. The energy balance is written for the $j+1$ time intervals.

$$(nH^E)_{j+1} = (nH^E)_j + n_{2,c}(\Delta H_2^v) - n_{1,v}(\Delta H_1^v) +$$

$$W_h + (W_b + W_s - Q) - \left[\left(\frac{nZg}{g_c}\right)_{j-1} - \left(\frac{nZg}{g_c}\right)_j\right] \quad (1)$$

[1] To whom correspondence should be addressed.

where g is the acceleration of gravity; g_c, gravitational constant; H^E, excess enthalpy; $\Delta H_2{}^v$, heat of vaporization of component 2 (initially charged component); $\Delta H_1{}^v$, heat of vaporization of component 1 (titrant component); j, $j+1$, subscripts denoting ends of successive time intervals; n, moles of liquid material in reaction vessel at any instant; $n_{2,c}$, moles of component 2 condensing during $j+1$ time interval (note that the net material condensed is pure component 2); $n_{1,v}$, moles of component 1 vaporizing during $j+1$ time interval (note that the net material vaporizing is pure component 1); Q, energy removed by Peltier cooler; W_{atm}, work of expansion against the atmosphere; W_b, electrical work (energy dissipated in thermistor beads); W_h, energy input to control heater; W_s, mechanical work input to stirrer; and Z, midpoint height of liquid in reaction vessel.

Besides the deletion of numerically negligible terms, Equation 1 assumes ideal gas behavior. The term in squared brackets in Equation 1 represents the incremental accumulation of energy in the form of potential energy of the system.

The $n_{1,v}$ and $n_{2,c}$ terms in Equation 1 were obtained from mass balances around the vapor phase. For component 1 (the titrant material)

$$n_{1,v} = n_{1,d} + [(n_1{}^V)_{j+1} - (n_1{}^V)_j]\qquad(2)$$

For component 2 (the initially charged material)

$$O = n_{2,d} + n_{2,c} + [(n_2{}^V)_{j+1} - (n_2{}^V)_j]\qquad(3)$$

For air

$$O = n_{air,d} + [(n_{air}{}^V)_{j+1} - (n_{air}{}^V)_j]\qquad(4)$$

The subscript d denotes material displaced from the reaction vessel, and the superscript V denotes the vapor phase. It was assumed that the composition of the displaced vapor was the average composition for that interval or

$$n_{i,d} = n_d\left[\frac{(y_i)_{j+1} + (y_i)_j}{2}\right]\qquad(5)$$
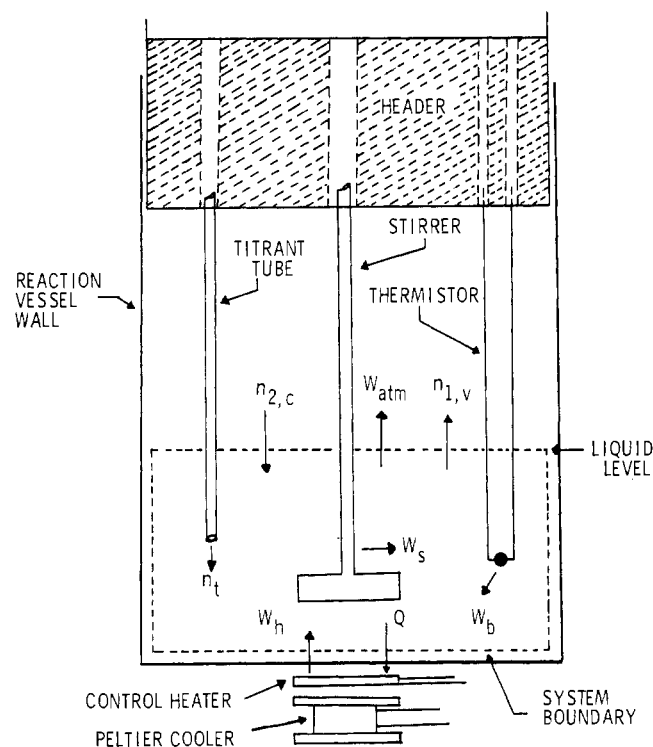

Figure 1. Various energies and masses involved in energy balance around liquid phase in reaction vessel

The vapor mole fractions (y_i) were calculated from the known liquid mole fractions (x_i) by assuming equilibrium between the two phases at all times and using the van Laar equation to predict the activity coefficients. The van Laar constants were obtained from experimental vapor-liquid equilibrium data when available and from predicted infinite dilution activity coefficients in other cases. The use of Equation 5 in Equation 4 permits the calculation of n_d, the total moles displaced during the $j+1$ interval. The $n_{1,v}$ and $n_{2,c}$ terms can then be obtained from Equations 2 and 3.

Other assumptions involved in the evaluation of the energy balance were complete mixing in both phases, negligible molecular diffusion of organic material out of the reaction vessel, a linear change in the base line value ($W_b + W_s - Q$) before and after the titration period, and an equality between the volume of entering titrant and the volume of displaced vapor in each time interval. With the exception of the last one, all of the assumptions could be checked in one way or the other and were essentially correct. The equilibrium and complete mixing assumptions were checked by varying the titration rate over a wide range. The linearity of the base line during the titration period was established by titrating a pure component into itself by use of pulsed injections and then noting the shift in the base line after each injection. Calculations were sufficient to show that molecular diffusion out of the reaction vessel was not a problem.

In the final analysis, only the assumption that the entering titrant displaces an equal volume of vapor appeared to be seriously inaccurate, and it was concluded that the failure of the above model for relatively volatile systems was due to that assumption. Evidently, a small amount of the vapor assumed to be displaced actually condenses. Initially, it was thought that this condensation occurred just after the titration started because of the pressure increase necessary to maintain steady flow of vapor through the orifices in the reaction vessel top. However, several titrations in which a pure component was titrated into itself indicated a small energy release owing to condensation throughout the titration period.

Acid-Base Titration

The accuracy of the calorimeter and the adequacy of the above process model for nonvolatile systems were established by measuring the heat of ionization of water at 25°C. This was done by titrating 0.0965N perchloric acid into 0.009576N sodium hydroxide and then correcting to infinite dilution conditions. The measured heat of neutralization was 13,452 cal mol^{-1}, which when corrected to infinite dilution gave $-13,382$ cal mol^{-1} for the ionization of water. This value compares well with the "best value" of $-13,345$ selected by Parker (7). The largest errors associated with the measurement were in the determination of the acid and base concentrations.

Cyclohexane-n-Hexane System

The cyclohexane-n-hexane system at 25°C has been suggested by McGlashan and Stoeckli (4) as a standard for checking heat of mixing calorimeters, and the excess enthalpy of that system has been firmly established by measurements in five different laboratories (3, 4, 6, 8, 9) by use of closed reaction vessels. The open reaction vessel consistently gave low H^E values, about 2.7% low when compared specifically with those of Marsh and Stokes (3).

An error analysis, in which each of the parameters entering into the calculations were perturbed individually to determine the effect on the calculated H^E values,
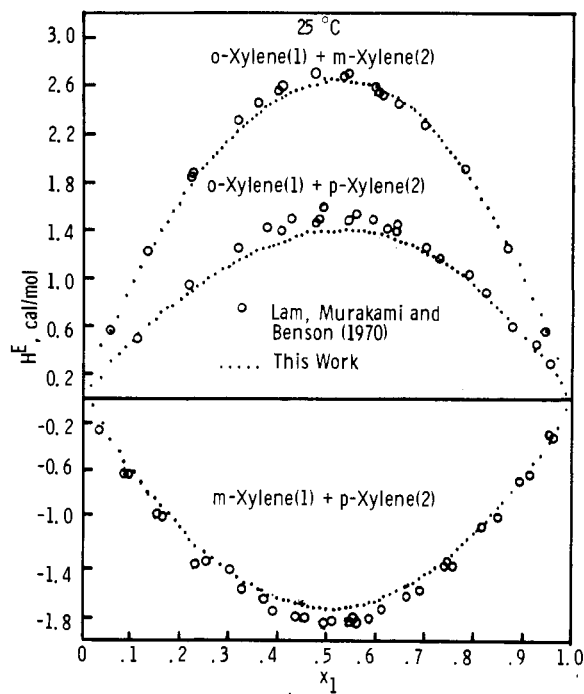
Figure 2. Comparison of new data for xylene isomer binaries at 25°C with that of Lam et al. (2)
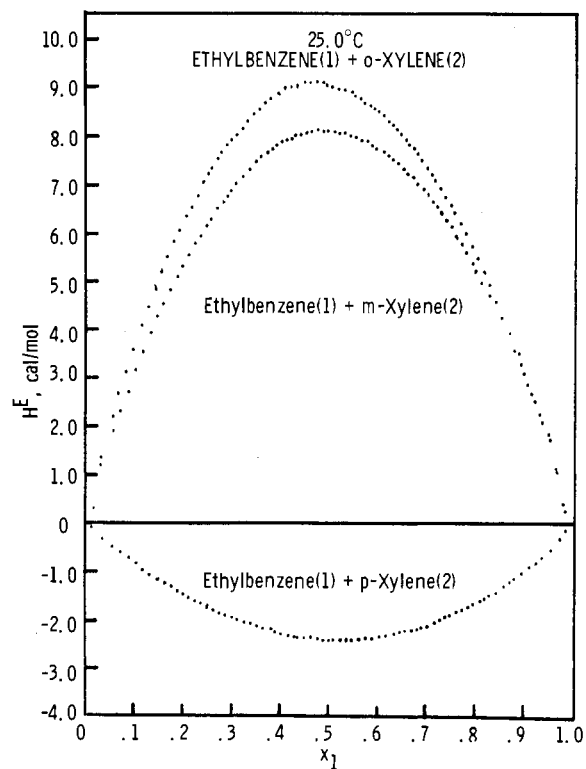

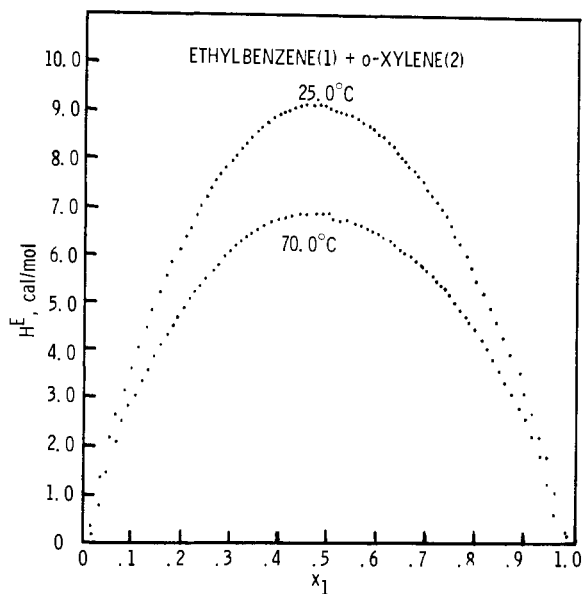**Figure 3.** New H^E data for ethylbenzene–xylene binaries at 25°C

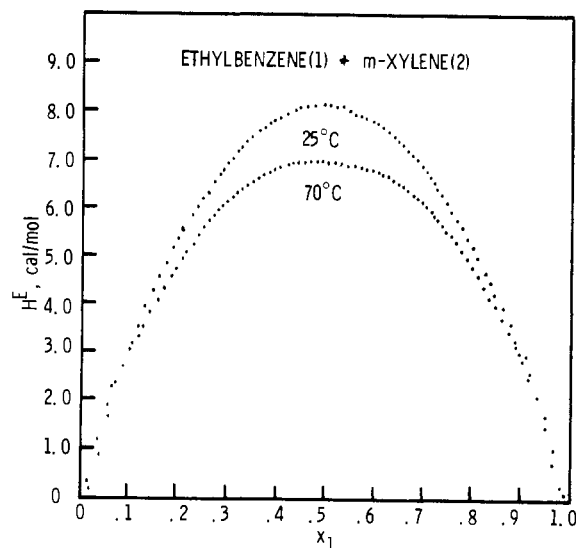**Figure 4.** Effect of temperature on H^E for ethylbenzene–o-xylene binary

Figure 5. Effect of temperature on H^E for ethylbenzene–m-xylene binary

showed that the error was not due to possible errors in the values used for the activity coefficients, heats of vaporization, vapor pressures, liquid densities, titration rate, or the reaction vessel volume. The error lay in the evaluation of the difference

$$n_{2,c}(\Delta H_2^v) - n_{1,c}(\Delta H_1^v)$$

in Equation 1. Equations 2–5, which assume that the volume of vapor displaced equals the volume of entering titrant, do not give sufficiently accurate values of $n_{1,v}$ and $n_{2,c}$ for systems as volative as the cyclohexane–n-hexane system at 25°C.

Benzene–Cyclohexane System

The open reaction vessel gave much better results for the less volatile benzene–cyclohexane system at 35°C. The data of Mrazek and Van Ness (5) were reproduced well within 1%. At 35°C these two compounds have volatilities close to that of n-hexane at 25°C. However, the midpoint H^E is about 18.7 cal mol^{-1} for benzene–cyclohexane at 35°C compared to about 52.9 cal mol^{-1} for cyclohexane–n-hexane at 25°C. The error owing to the vapor space, which caused a 2.7% error in the latter system, caused less than 1% error in the former.

Table I. Excess Enthalpy Data for C₈ Aromatic Binaries

Tabulated H^E values are in cal/mol where 1 cal = 4.184 J

Ethylbenzene(1)+p-xylene(2) at 25°C

x_1	H^E	x_1	H^E	x_1	H^E
0.0365	−0.30	0.3914	−2.20	0.6638	−2.14
0.0703	−0.58	0.4117	−2.24	0.6961	−2.04
0.1019	−0.81	0.4427	−2.29	0.7224	−1.94
0.1314	−1.02	0.4706	−2.32	0.7509	−1.82
0.1722	−1.27	0.4958	−2.34	0.7816	−1.67
0.2094	−1.49	0.5011	−2.34	0.8150	−1.48
0.2433	−1.66	0.5389	−2.33	0.8513	−1.25
0.2745	−1.81	0.5655	−2.31	0.8911	−0.96
0.3122	−1.96	0.6011	−2.27	0.9347	−0.61
0.3542	−2.10	0.6344	−2.21	0.9663	−0.28

Ethylbenzene(1)+m-xylene(2) at 25°C

x_1	H^E	x_1	H^E	x_1	H^E
0.0364	1.19	0.3845	7.82	0.6725	7.12
0.0704	2.28	0.4184	8.02	0.7068	6.70
0.1020	3.16	0.4430	8.11	0.7349	6.31
0.1315	3.92	0.4813	8.17	0.7653	5.82
0.1723	4.85	0.5101	8.15	0.7984	5.23
0.2095	5.59	0.5359	8.08	0.8344	4.52
0.2435	6.18	0.5412	8.04	0.8739	3.65
0.2845	6.80	0.5749	7.91	0.9023	2.92
0.3213	7.25	0.6130	7.67	0.9327	2.14
0.3465	7.51	0.6414	7.44	0.9651	1.08

Ethylbenzene(1)+m-xylene(2) at 70°C

x_1	H^E	x_1	H^E	x_1	H^E
0.0353	0.86	0.3696	6.72	0.6652	6.37
0.0682	2.33	0.4040	6.88	0.6986	6.07
0.0990	3.04	0.4406	6.97	0.7259	5.78
0.1278	3.57	0.4731	6.98	0.7555	5.42
0.1677	4.32	0.5064	6.92	0.7989	4.79
0.1923	4.73	0.5121	6.92	0.8349	4.19
0.2267	5.24	0.5420	6.93	0.8607	3.71
0.2681	5.85	0.5757	6.86	0.9026	2.94
0.3054	6.24	0.6005	6.76	0.9329	2.19
0.3309	6.46	0.6348	6.59	0.9652	0.77

Ethylbenzene(1)+o-xylene(2) at 25°C

x_1	H^E	x_1	H^E	x_1	H^E
0.0349	1.32	0.4014	8.96	0.6576	7.89
0.0676	2.68	0.4437	9.10	0.6928	7.40
0.0980	3.61	0.4652	9.13	0.7319	6.80
0.1266	4.48	0.4852	9.12	0.7642	6.22
0.1662	5.53	0.4899	9.02	0.7996	5.49
0.2024	6.35	0.5092	8.98	0.8383	4.63
0.2460	7.20	0.5300	8.92	0.8663	3.96
0.2851	7.82	0.5646	8.75	0.9120	2.71
0.3203	8.28	0.5903	8.56	0.9453	1.84
0.3671	8.73	0.6259	8.24	0.9628	1.10

Ethylbenzene(1)+o-xylene(2) at 70°C

x_1	H^E	x_1	H^E	x_1	H^E
0.0324	0.70	0.3826	6.71	0.6798	5.85
0.0627	2.06	0.4187	6.84	0.7151	5.49
0.0913	2.82	0.4456	6.88	0.7440	5.15
0.1181	3.34	0.4702	6.89	0.7753	4.73
0.1673	4.30	0.5054	6.83	0.8094	4.22
0.2007	4.87	0.5102	6.70	0.8338	3.82
0.2414	5.46	0.5349	6.68	0.8734	3.12
0.2781	5.88	0.5799	6.54	0.9019	2.60
0.3114	6.21	0.6053	6.40	0.9324	1.86
0.3489	6.52	0.6404	6.17	0.9650	0.61

o-Xylene(1)+p-xylene(2) at 25°C

x_1	H^E	x_1	H^E	x_1	H^E
0.0351	0.17	0.4146	1.34	0.6558	1.32
0.0677	0.36	0.4442	1.37	0.6957	1.25
0.0983	0.49	0.4759	1.40	0.7313	1.17
0.1405	0.66	0.4838	1.40	0.7708	1.06
0.1910	0.83	0.5007	1.42	0.8147	0.92
0.2359	0.97	0.5189	1.42	0.8511	0.78
0.2665	1.05	0.5384	1.43	0.8909	0.62
0.3036	1.14	0.5650	1.42	0.9196	0.48
0.3450	1.23	0.5944	1.40	0.9346	0.41
0.3818	1.29	0.6270	1.36	0.9662	0.24

o-Xylene(1)+m-xylene(2) at 25°C

x_1	H^E	x_1	H^E	x_1	H^E
0.0178	0.11	0.4015	2.51	0.6579	2.44
0.0516	0.56	0.4438	2.58	0.6820	2.36
0.0981	0.97	0.4601	2.60	0.7264	2.17
0.1267	1.19	0.4804	2.61	0.7664	1.97
0.1663	1.47	0.4859	2.66	0.7993	1.78
0.2024	1.70	0.5035	2.67	0.8479	1.44
0.2461	1.94	0.5273	2.67	0.8884	1.13
0.2851	2.13	0.5590	2.64	0.9177	0.86
0.3204	2.27	0.5885	2.60	0.9489	0.61
0.3672	2.43	0.6282	2.52	0.9653	0.36

m-Xylene+p-xylene(2) at 25°C

x_1	H^E	x_1	H^E	x_1	H^E
0.0358	−0.22	0.3871	−1.60	0.6472	−1.56
0.0692	−0.45	0.4202	−1.64	0.6791	−1.49
0.1003	−0.60	0.4608	−1.68	0.7144	−1.39
0.1433	−0.81	0.4865	−1.69	0.7535	−1.27
0.1945	−1.04	0.5008	−1.70	0.7972	−1.10
0.2291	−1.18	0.5190	−1.71	0.8334	−0.94
0.2609	−1.29	0.5290	−1.70	0.8731	−0.75
0.3084	−1.43	0.5447	−1.69	0.9017	−0.59
0.3422	−1.51	0.5791	−1.66	0.9483	−0.34
0.3655	−1.56	0.6045	−1.63	0.9649	−0.21

C₈ Aromatic Systems

The calorimeter was tested next on the C₈ aromatic binaries at 25° and 70°C. At those two temperatures, the vapor pressures of ethylbenzene are about 6.3 and 56% of those of n-hexane at 25°C. The analogous ratios for o-xylene are 0.44 and 4.2%. Hence, the vapor space error should be negligible for the C₈ aromatics at 25°C and of minor importance at 70°C.

The new data for the xylene isomer binaries at 25°C are compared with those of Lam et al. (2) in Figure 2. The average difference in the midpoint values for the two sets of data is only 0.09 cal mol⁻¹. It is believed that the error owing to the vapor space is negligible for the C₈ aromatics at 25°C. If the differences between the two sets of data in Figure 2 were due to the vapor space error, the new data for the system with the negative H^E values would have fallen below (more negative) the data of Lam et al. as it does for the two systems with positive H^E values.

New data for the three ethylbenzene–xylene systems at 25°C are shown in Figure 3. The effect of temperature on two ethylbenzene–xylene systems is shown in Figures 4 and 5. The effect of the vapor space error on the accuracy of the 70°C data cannot be determined by comparison with other data but is believed to be small enough to permit the reported data to be used with confidence until it can be verified with a closed vessel.

Two runs were required to establish each of the binary curves shown in Figures 2–5. The experimental program was such that the two half curves were run several days apart in time. A requirement was set that the two half curves had to match within 1% for the two runs to be acceptable.

Time intervals of 20 sec were used; this produced about 60 data points per half-curve. Only enough of the points is shown in the figures to define the curves. The tabulations of the experimental data in Table I include only 30 points per binary curve.

Summary

The accuracy of a new Tronac isothermal titration cal-
orimeter with an open reaction vessel has been verified
for nonvolatile systems by duplicating the accepted value
for the ionization of water within 0.38%. Despite an at-
tempt to develop a process model which would accurate-
ly correct for the effect of the vapor space in the reaction
vessel, the results for the cyclohexane–n-hexane system
at 25°C were about 2.7% below the accepted midpoint
value (52.9 cal mol^{-1}) for this standard system. For the
benzene–cyclohexane system at 35°C, the error owing to
the vapor space amounted to less than 1% in the mea-
sured midpoint value of 187 cal mol^{-1}.

New H^E data for the three xylene–xylene binaries at
25°C closely reproduced the values reported previously
by Lam et al. (2). Other new data for the three ethylben-
zene–xylene binaries at 25°C and for two ethylbenzene-
xylene binaries at 70°C are presented. Because of the
low volatility of these systems, these data are believed to
be quite accurate despite the presence of the vapor
space in the reaction vessel.

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Vapor-Liquid Equilibrium Data for System Tri-n-butyl Phosphate and Sulfur Dioxide

David F. Cooper and James W. Smith[1]

Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ont. M5S 1A4, Canada

Equilibrium concentrations of sulfur dioxide over solutions
in tri-n-butyl phosphate were measured in the vapor
concentration range of 10–650 mm Hg and a
temperature range of 6–70°C. The data were correlated
by using a Henry's law model for the vapor-liquid
equilibrium and postulating a one-to-one complex in the
liquid phase. Spectroscopic evidence of an atomic
interaction of the sulfur dioxide and phosphoryl oxygen of
the phosphate is presented. The resulting equations
correlated the observed data with an average error of
under 3%, indicating that this model was useful for
interpolation of the data within the experimental range.
These equations were used to construct a table of
equilibrium data over the range of variables investigated
and to compare sulfur dioxide partial pressures over TBP
to those over water.

The recent increase in public awareness of ecological
problems resulting from man-made wastes being inade-
quately treated before their return to the environment has
placed an increased pressure on industry to limit its out-
put of possible pollutants. In the area of air pollution the
major pollutant in many industries is sulfur dioxide. One
common method for the removal of sulfur dioxide is ab-
sorption. Unfortunately, sulfur dioxide has a low solubility
in most inexpensive absorbants, and most solvents in
which sulfur dioxide is reasonably soluble are either ex-
pensive or difficult to work with.

Tri-n-butyl phosphate (TBP) is a nontoxic, noncorrosive
chemical commercially available in large quantities at
moderate cost. It has a high boiling point, (289°C) and at
moderate temperatures the vapor pressure is relatively
low (about 0.1 mm Hg at 60°C). Many researchers have

suggested the use of TBP as an absorbant for sulfur-con-
taining gases such as hydrogen sulfide and sulfur dioxide
(3, 4, 6-8). To help evaluate TBP as an absorbant for
sulfur dioxide, a program to measure the vapor-liquid
phase equilibrium of this system was undertaken.

This paper reports phase equilibrium data for the
TBP–sulfur dioxide system over the range 6–70°C and for
partial vapor pressures of sulfur dioxide from 10 to 650
mm Hg. A model that assumes a one-to-one complex of
the TBP and sulfur dioxide is used to correlate this data,
and infrared spectroscopic evidence of an interaction of
the sulfur dioxide with the phosphoryl oxygen of the TBP
will be presented. This model was used to calculate equi-
librium data over the range studied and has been com-
pared with similar data for the system sulfur dioxide-
water (12).

Experimental

The TBP used in this study was BDH reagent grade
and by standard Karl Fischer analysis, it contained 0.099
wt % water. The sulfur dioxide was obtained from Mathe-
son of Canada Ltd., and was 99.9% pure.

The phases were equilibrated in a cylindrical flask (vol-
ume 125 cc) constructed of glass. The volume of liquid
was usually about 25 cc. This flask was constructed so
that sulfur dioxide could be added through a sparger, and
gas sampling could be done with the flask completely im-
mersed in the water bath. During equilibration the flask
was open to the atmosphere through a fine capillary tube
about 10 cm long with a bulb (volume about 2 cc) near
the lower end. Experiments were done at an atmospheric
pressure of 757 mm Hg (±3 mm Hg). The experimental
procedure was as follows:

A known weight of TBP was placed in the flask, and
the flask closed and placed in a water bath (±0.1°C).
After thermal equilibration the flask was dried and
weighed at a fixed time after removal from the bath. All
later weighings were done by using this procedure. The