can be estimated by minimizing the Gibbs free energy by the UNIFAC method.

Table VI shows all interaction parameter values used in the LLE estimation. Prediction of the LLE on these systems by the UNIFAC method showed a correct qualitative behavior regarding mutual solubilities, but gave a poor quantitative agreement with the experimental data. This is more evident for the system containing BA (see Figure 3), probably due to inappropriate figures for the interaction parameters used for the calculation and the fact that the UNIFAC model had not taken into account the interaction between the OH groups of both alcohols in the solution for LLE calculation.

Glossary

AA	amyl acetate
BA	benzyl alcohol
MIK	methyl isobutyl ketone
m_2	distribution coefficient of ethanol ($m_2 = W_{23}/W_{21}$)
PP	plait point
W_{11}	weight fraction of water (1) in the water-rich layer
W_{13}	weight fraction of water (1) in the solvent-rich layer
W_{21}	weight fraction of ethanol (2) in the water-rich layer
W_{23}	weight fraction of ethanol (2) in the solvent-rich layer
W_{31}	weight fraction of solvent (3) in the water-rich layer
W_{33}	weight fraction of solvent (3) in the solvent-rich layer

Registry No. AA, 628-63-7; MIK, 108-10-1; BA, 100-51-6; ethanol, 64-17-5.

Literature Cited

(1) Roddy, J. W. *Ind. Eng. Chem. Process Des. Dev.* **1981**, *20*, 104-107.
(2) Roddy, J. W.; Coleman, C. F. *Ind. Eng. Chem. Fundam.* **1981**, *20*, 250-254.
(3) Fredenslund, Aa.; Gmehling, J.; Rasmussen, P. *Vapor-Liquid Equilibria Using UNIFAC*; Elsevier: Amsterdam, 1977; pp 27-64 and 243-249.
(4) Magnussen, T.; Rasmussen, P.; Fredenslund, Aa. *Ind. Eng. Chem. Process Des. Dev.* **1981**, *20*, 331-339.
(5) Magnussen, T. Phase Equilibria and Separation Process; Instituttet for Kemiteknik, Denmark; MAN 8001, 1980.
(6) Riddick, J. A.; Bunger, W. B. *Organic Solvents*; Weissberger, A., Ed. Wiley-Interscience: New York, 1970; Vol. II.
(7) Weast, R. C. *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 1980-1981.
(8) Othmer, D. F.; Tobias, P. E. *Ind. Eng. Chem.* **1942**, *34*, 690-700.
(9) Treybal, R. E. *Liquid Extraction*; McGraw-Hill: New York, San Francisco, Toronto, and London, 1963; pp 122-127.
(10) Sørensen, J.; Magnussen, T.; Rasmussen, P.; Fredenslund, Aa. *Fluid Phase Equilib.* **1979**, *2*, 297.
(11) Sørensen, J. M.; Magnussen, T.; Rasmussen, P.; Fredenslund, Aa. *Fluid Phase Equilib.* **1979**, *3*, 47.
(12) Sørensen, J. M.; Magnussen, T.; Rasmussen, P.; Fredenslund, Aa. *Fluid Phase Equilib.* **1980**, *4*, 151.

Received for review March 31, 1988. Accepted September 21, 1988. We are grateful to SECYT, Repûblica Argentina, for financial support.

Vapor-Liquid Equilibria at 760 mmHg in the Binary Systems Cyclohexene-1,2-Dichloroethane and Cyclohexane-1,2-Dichloroethane

Fidel Mato,* Gerardo Gonzalez, and Francisco J. Arroyo
Department of Chemical Engineering, University of Valladolid, Valladolid, Spain 47005

Vapor-liquid equilibrium at 1 atm pressure has been determined for the title binary systems. Thermodynamic consistency was checked by Herington's area test. Both systems present moderate positive deviations from ideal behavior, and minimum boiling azeotropes were observed. The data were satisfactorily correlated by various equations, and appropriate parameters are reported.

Introduction

The vapor-liquid equilibria (VLE) for the three binary systems cyclohexene-1,2-dichloroethane, cyclohexane-1,2-dichloroethane, and cyclohexene-cyclohexane have been investigated by Mesnage and Marsan (*1*) inasmuch as the previously reported data (*2*, *3*) for the systems cyclohexane-1,2-dichloroethane and cyclohexene-cyclohexane showed an inadequate thermodynamic consistency. However, the data of Mesnage and Marsan (*1*) for the systems cyclohexene-1,2-dichloroethane and cyclohexane-1,2-dichloroethane also show a doubtful thermodynamic consistency according to the Herington (*4*) criterion; on the other hand, opposite to indications by Mesnage and Marsan, the van Laar equation correlates the experimental data as well as the Wilson equation.

The aim of this paper is to provide new VLE data for the systems cyclohexene-1,2 dichloroethane and cyclohexane-1,2 dichloroethane at the pressure of 1 atm. The experimental data of this work satisfy the consistency test of Herington and can be satisfactorily correlated by the van Laar, Mato, Wilson, and NRTL equations.

Experimental Section

Purity of Materials. All starting chemicals were distilled through a column (20 mm i.d. and 900 mm long) packed with 2 × 2 mm Dixon rings. The final purity level of all chemicals, estimated by gas-liquid chromatography, was better than 99.85%, and some significant physical properties (density, refractive index, and boiling point) are listed in Table I along with the literature values.

Apparatus and Procedure. The VLE data were obtained by use of an all-glass recirculation still connected to a constant-pressure system operated at 760 ± 0.1 mmHg. The equilibrium temperatures were measured with a certified mercury thermometer (PROTON). The accuracy in determination of temperature was ±0.1 °C. The apparatus and the experimental features have been described in detail elsewhere (*5*).

The liquid and condensed vapor compositions were obtained from density measurements at 25 °C by using a double leveling pycnometer. Previous calibration analysis was carried out with mixtures of known composition. Molar fractions of the mixtures

---

* To whom correspondence should be addressed.

0021-9568/89/1734-0179$01.50/0 © 1989 American Chemical Society

Table I. Physical Properties of Chemicals

		density, g/cm^3, at 25 °C		refract. index at 25 °C		bp, °C	
component	supplier	exptl	lit.[a]	exptl	lit.[a]	exptl	lit.[a]
cyclohexene	Fluka	0.8058	0.80609	1.4439	1.44377	83.00	82.979
cyclohexane	Merck	0.7737	0.77389	1.4235	1.42354	80.75	80.725
1,2-dichloroethane	Panreac	1.2457	1.2458	1.4422	1.4421	83.50	83.483

[a] Reference *13*.

Table II. Vapor-Liquid Equilibrium Data for Cyclohexene (1)-1,2-Dichloroethane (2) at 760 mmHg

x_1	y_1	T	ϕ_1	ϕ_2	γ_1	γ_2
0.0600	0.0850	82.5	0.9665	0.9708	1.4339	0.9951
0.0825	0.1160	82.1	0.9664	0.9707	1.4403	0.9971
0.1165	0.1570	81.5	0.9663	0.9705	1.4034	1.0042
0.1500	0.1995	81.0	0.9661	0.9704	1.4081	1.0081
0.1975	0.2545	80.4	0.9660	0.9703	1.3893	1.0130
0.2420	0.2900	80.1	0.9659	0.9702	1.3038	1.0309
0.2725	0.3200	79.9	0.9658	0.9701	1.2854	1.0351
0.3065	0.3555	79.5	0.9657	0.9701	1.2851	1.0422
0.3375	0.3840	79.4	0.9656	0.9700	1.2644	1.0459
0.3970	0.4280	79.2	0.9655	0.9700	1.2053	1.0737
0.4425	0.4670	79.2	0.9655	0.9700	1.1817	1.0839
0.4850	0.4960	79.1	0.9654	0.9700	1.1468	1.1112
0.5100	0.5150	79.1	0.9654	0.9700	1.1341	1.1256
0.5635	0.5545	79.1	0.9653	0.9700	1.1050	1.1607
0.5875	0.5700	79.1	0.9653	0.9700	1.0878	1.1836
0.6510	0.6225	79.3	0.9653	0.9700	1.0655	1.2205
0.7010	0.6595	79.5	0.9653	0.9701	1.0419	1.2770
0.7315	0.6910	79.8	0.9654	0.9701	1.0367	1.2785
0.7525	0.7060	79.9	0.9654	0.9701	1.0265	1.3155
0.8150	0.7660	80.4	0.9655	0.9702	1.0128	1.3792
0.9025	0.8675	81.5	0.9656	0.9704	1.0018	1.4323
0.9495	0.9240	82.1	0.9658	0.9705	0.9947	1.5547

Table III. Vapor-Liquid Equilibrium Data for Cyclohexane (1)-1,2-Dichloroethane (2) at 760 mmHg

x_1	y_1	T	ϕ_1	ϕ_2	γ_1	γ_2
0.0650	0.1460	80.5	0.9649	0.9703	2.2603	0.9945
0.0825	0.1700	80.0	0.9648	0.9702	2.1017	0.9988
0.1200	0.2370	78.8	0.9645	0.9699	2.0916	0.9953
0.1730	0.2980	77.6	0.9641	0.9696	1.8858	1.0086
0.2150	0.3340	77.0	0.9639	0.9695	1.7347	1.0291
0.2615	0.3750	76.4	0.9637	0.9694	1.6309	1.0463
0.3190	0.4080	75.9	0.9635	0.9693	1.4770	1.0920
0.3610	0.4360	75.6	0.9634	0.9692	1.4077	1.1193
0.4295	0.4760	75.2	0.9633	0.9691	1.3057	1.1779
0.5170	0.5250	75.1	0.9631	0.9691	1.2018	1.2673
0.5245	0.5300	75.1	0.9631	0.9691	1.1959	1.2738
0.5610	0.5510	75.1	0.9631	0.9691	1.1606	1.3159
0.5975	0.5710	75.2	0.9631	0.9692	1.1275	1.3692
0.7290	0.6560	75.7	0.9631	0.9693	1.0436	1.6022
0.8200	0.7350	76.6	0.9632	0.9695	1.0142	1.8116
0.8800	0.7980	77.5	0.9634	0.9697	0.9966	2.0099
0.9550	0.9150	79.3	0.9637	0.9700	0.9955	2.1280

were estimated to be within ±0.0005 accuracy for both phases, which indicates a more precise analysis method than the gas-chromatography method used by Mesnage and Marsan (*1*).

Results

The VLE data of this work for the systems cyclohexene-1,2-dichloroethane and cyclohexane-1,2-dichloroethane at 760 mmHg are reported in Tables II and III and are also plotted in Figures 1 and 2 together with literature data points (*2*, *3*).

Liquid-phase activity coefficients were calculated by the equation

$$\gamma_i = (y_i \phi_i P)/(x_i f^\circ_i) \qquad (1)$$

Vapor-phase nonidealities were calculated, with equivalent results, by using the Peng and Robinson (*6*) equation of state and from the virial equation, truncated after the second term,

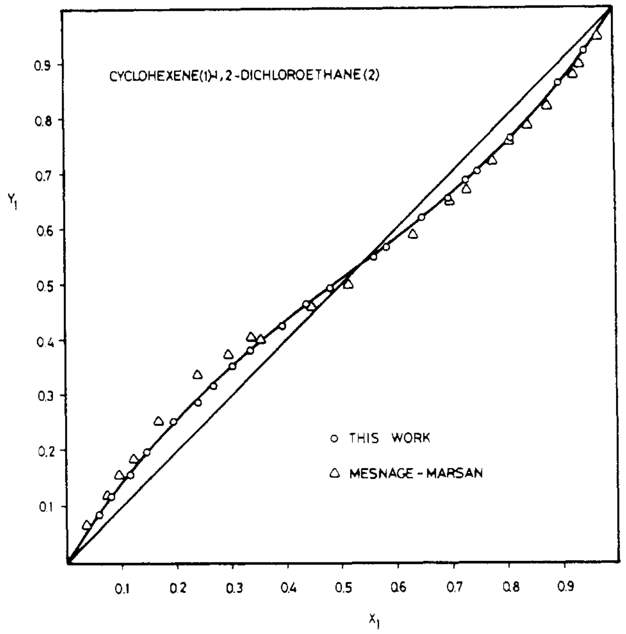

Figure 1. *x-y* diagram for the binary system cyclohexene (1)-1,2-dichloroethane (2) at 760 mmHg.

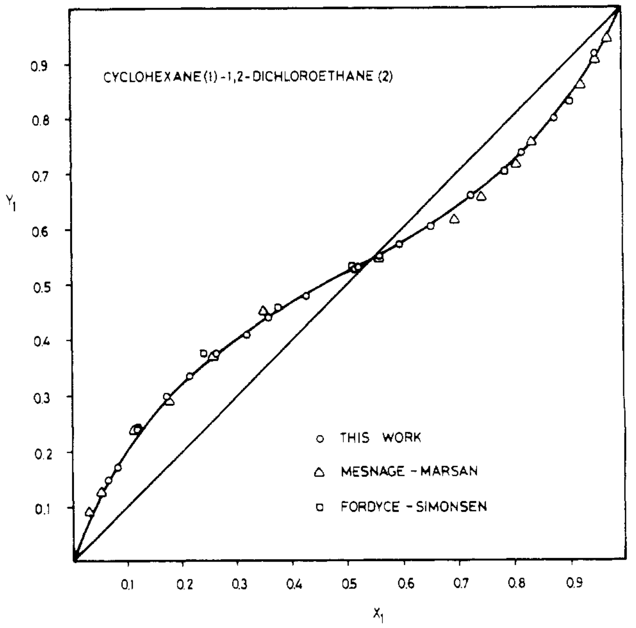

Figure 2. *x-y* diagram for the binary system cyclohexane (1)-1,2-dichloroethane (2) at 760 mmHg.

Table IV. Antoine Constants[a] for Pure Compounds

	α	β	γ
cyclohexene	6.886 17	1229.973	224.104
cyclohexane	6.844 98	1203.526	222.863
1,2-dichloroethane	7.046 36	1305.4	230

[a] $\log P^s = \alpha - \beta/(T + \gamma)$. Reference *13*.

Table V. Fitted Parameters from Data Correlation

	cyclohexene (1)–1,2-dichloroethane (2)			cyclohexane (1)–1,2-dichloroethane (2)		
	parameters[a]			parameters[a]		
model	Δ_{12}	Δ_{21}	Δy[b]	Δ_{12}	Δ_{21}	Δy[b]
van Laar	0.4383	0.5013	0.0025	0.9324	0.8388	0.0032
Mato	0.4374	0.5015	0.0025	0.9319	0.8381	0.0032
Wilson	0.8929	0.6728	0.0026	0.5332	0.6803	0.0037
NRTL	0.4792	0.0231	0.0025	0.2979	0.6635	0.0033

[a] van Laar: $\Delta_{12} = A_{12}$; $\Delta_{21} = A_{21}$. Mato: $\Delta_{12} = A$; $\Delta_{21} = B$. Wilson: $\Delta_{12} = \Lambda_{12}$; $\Delta_{21} = \Lambda_{21}$. NRTL: $\Delta_{12} = \tau_{12}$; $\Delta_{21} = \tau_{21}$; $\alpha = 0.3$. [b] $\Delta y = (\sum |y_{\text{exptl}} - y_{\text{calcd}}|)/N$.

with the second virial coefficients obtained by the method of Hayden and O'Connell (*7*). Values of ϕ_1 and ϕ_2 in Tables II and III are as calculated by the Peng and Robinson equation. Standard-state fugacities for the liquid phase at zero pressure were calculated from the correlation of Prausnitz et al. (*8*). Vapor pressures were calculated by using the Antoine equation with the constants listed in Table IV.

The experimental data were checked for thermodynamic consistency by using the Herington test (*4*). It can observed in Figures 3 and 4 that both systems present a good consistency test with area deviations below 2%.

These results are better than those obtained by Mesnage and Marsan (*1*) when they apply the same test. On the other hand, from the curves ln γ_1/γ_2 vs x_1 showed by these authors, it is not possible to determine with precision the areas and then to conclude on the thermodynamic consistency of these systems.

The experimental data were correlated by the van Laar (*9*), Mato (*10*), Wilson (*11*), and NRTL (*12*) equations. The activity coefficient equations of Mato equation for binary systems are

$$\ln \gamma_1 = A x_2^2 \frac{1 + (1 - (A/B)^{1/2}) x_1}{(x_2 + x_1 (A/B)^{1/2})^3}$$

$$\ln \gamma_2 = B x_1^2 \frac{1 + (1 - (B/A)^{1/2}) x_2}{(x_1 + x_2 (B/A)^{1/2})^3} \tag{2}$$

As recommended by Renon and Prausnitz (*12*), the mixture nonrandomness parameter α_{ij} was set as 0.3 in the NRTL equation.

The adjustable binary parameters of each model were estimated by a nonlinear regression model. The following objective function was minimized

$$\text{OF} = \sum_{i=1}^{N} \left[\left(\frac{\gamma_{1,\text{exptl}} - \gamma_{1,\text{calcd}}}{\gamma_{1,\text{exptl}}} \right)_i^2 + \left(\frac{\gamma_{2,\text{exptl}} - \gamma_{2,\text{calcd}}}{\gamma_{2,\text{exptl}}} \right)_i^2 \right] \tag{3}$$

These parameters are shown in Table V, along with the average deviation of the vapor compositions between the experimental and the fitted values. The results indicate that all equations are suitable to represent the data. Also, the azeotropic conditions predicted by the fitting equations, shown in Table VI, agree with the experimental values.

Opposite to indications by Mesnage and Marsan (*1*), the van Laar equation correlates the experimental data as well as the Wilson equation. We believe that this erroneous conclusion derived by Mesnage and Marsan is imputable to the imprecision of the experimental data in the regions of extreme compositions, because they did not use an adequate criterion of ponderation to evaluate the A_{12} and A_{21} adjustable parameters with the van Laar equation.

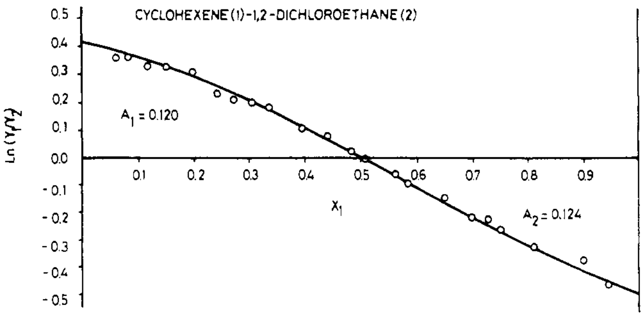

Figure 3. Herington consistency test for the binary system cyclohexene (1)–1,2-dichloroethane (2).

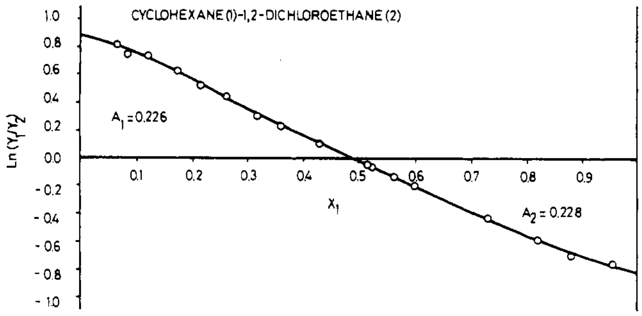

Figure 4. Herington consistency test for the binary system cyclohexane (1)–1,2-dichloroethane (2).

Therefore, considering the previously disclosed results, the results obtained in this work improve notably the available experimental VLE data for the systems cyclohexene–1,2-dichloroethane and cyclohexane–1,2-dichloroethane.

Glossary

A_{ij}	van Laar parameter
A, B	Mato parameters
f°_i	standard-state fugacity for the liquid phase
N	number of experimental points
P	total pressure
P^s	vapor pressure
T	temperature, °C
x_i	liquid mole fraction of component *i*
y_i	vapor mole fraction of component *i*

Greek Letters

α, β, γ	constants of the Antoine equation
α_{ij}	NRTL nonrandomness parameter
Λ_{ij}	Wilson parameter
τ_{ij}	NRTL parameter
ϕ_i	vapor-phase fugacity coefficient of component *i*
γ_i	liquid-phase activity coefficient of component *i*

Table VI. Experimental and Calculated Azeotropic Point

system	experimental	van Laar	Mato	Wilson	NRTL
cyclohexene (1)–1,2-dichloroethane (2)	$x_1 = 0.528$ $T = 79.1$ °C	$x_1 = 0.532$ $T = 79.4$ °C	$x_1 = 0.533$ $T = 79.4$ °C	$x_1 = 0.532$ $T = 79.4$ °C	$x_1 = 0.533$ $T = 79.4$ °C
cyclohexane (1)–1,2-dichloroethane (2)	$x_1 = 0.536$ $T = 75.1$ °C	$x_1 = 0.537$ $T = 74.9$ °C	$x_1 = 0.537$ $T = 74.9$ °C	$x_1 = 0.538$ $T = 75.0$ °C	$x_1 = 0.535$ $T = 74.9$ °C

Registry No. Cyclohexene, 110-83-8; cyclohexane, 110-82-7; 1,2-dichloroethane, 107-06-2.

Literature Cited

(1) Mesnage, J.; Marsan, A. A. *J. Chem. Eng. Data* **1971**, *16*, 434.
(2) Fordyce, C. T.; Simonsen, D. R. *Ind. Eng. Chem.* **1949**, *41*, 104.
(3) Harrison, J. M.; Lloyd, B. *Ind. Eng. Chem.* **1946**, *38*, 117.
(4) Herington, E. F. G. *J. Inst. Pet.* **1951**, *37*, 457.
(5) Mato, F.; Cepeda, E. *An. Quim.* **1984**, *80*, 338.
(6) Peng, D.; Robinson, D. B. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59.
(7) Hayden, J. G.; O'Connell, J. P. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209.
(8) Prausnitz, J. M.; Eckert, C. A.; Orye, R. V.; O'Connell, J. P. *Computer Calculations for Multicomponent Vapor-Liquid Equilibria*; Prentice Hall: Englewood Cliffs, NJ, 1967.
(9) van Laar, J. J. *Z. Phys. Chem.* **1910**, *72*, 273.
(10) Mato, F.; Mato, F. A. *Fluid Phase Equilib.* **1985**, *20*, 183.
(11) Wilson, G. M. *J. Am. Chem. Soc.* **1964**, *86*, 127.
(12) Renon, H.; Prausnitz, J. M. *AIChE J.* **1968**, *14*, 135.
(13) Riddick, J. A.; Bunger, W. B. *Organic Solvents*; Wiley-Interscience: New York, 1970.

Received for review February 21, 1986. Revised April 13, 1987. Accepted February 27, 1988.

Molality Dependence of the Differential Enthalpies of Solution of RbBr in Water at 298.15 K

Anna Sanahuja* and Juan L. Gômez-Estêvez

Departament de Física Fonamental, Facultat de Física, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain

The differential enthalpies of solution of RbBr in water at 298.15 K were measured in the molality range 0.1–5.0 mol kg^{-1}. The experimental system was a Tian-Calvet calorimeter type adapted to this particular case and tested in previous works. From the experimental results the molality dependence of the relative apparent molar enthalpy $L_\phi(m)$ has been obtained up to 5.0 mol kg^{-1}.

Introduction

There is in general a lack of information about the enthalpies of the aqueous solutions of rubidium halides and RbBr in particular (1–3). In a previous work (*4*), the enthalpies of solution of RbBr in water at 298.15 K and at low molalities (<0.071 mol kg^{-1}) were measured. From the measurements and the literature data the enthalpy of solution at infinite dilution was obtained (*4*).

With respect to the molality dependence of the enthalpy of the aqueous solutions of RbBr, the situation is worse. The only experimental study until now has been made by Fortier et al. (*5*). They measured the enthalpies of dilution in the molality range 0.04–0.96 mol kg^{-1} by using a Picker microcalorimeter, and the molality dependence of the relative apparent molar enthalpy $L_\phi(m)$ was obtained.

The purpose of this work was to extend our knowledge of the L_ϕ's to higher molalities. The method employed was based on the experimental determination of the differential enthalpies of solution $\Delta_{sol}H_2$ of RbBr in water at 298.15 K. The molality range covered was from 0.1 to 5.0 mol kg^{-1}. The obtention of L_ϕ from $\Delta_{sol}H_2$ was developed and tested in two previous works (*6*, *7*) for NaCl and KCl aqueous solutions in water at 298.15 K in the whole molality range.

Experimental Section

The differential enthalpies of solution were measured with a Tian-Calvet calorimeter type described in detail in previous works (*6*, *8*). The experimental procedure was described previously (*6*).

For each measurement of the differential enthalpy of solution the temperature was determined within ±0.02 K, an electrical calibration was carried out before and after each solution process, and the initial mechanical effect was corrected as explained earlier (*6*). The calorimetric resolution is 0.02 J and the reproducibility of the measurements is better than 1%.

Table I. Calorimetric Differential Enthalpies of Solution of RbBr in Water at 298.15 K

m, mol kg^{-1}	Δm, mol kg^{-1}	T, K	$\Delta_{sol}H_2^{exptl}(T)$, J mol^{-1}	$\Delta_{sol}H_2^{exptl}$(298.15 K), J mol^{-1}	ϵ, J mol^{-1}
0.100 33	0.013 80	298.30	22 196	22 223	27
0.116 54	0.023 54	298.12	22 401	22 396	13
0.202 99	0.019 43	298.12	22 221	22 216	92
0.306 96	0.021 06	298.12	22 054	22 049	35
0.502 66	0.020 40	298.25	21 384	21 400	17
0.700 98	0.017 07	298.25	21 179	21 195	40
0.705 59	0.019 82	298.47	21 150	21 167	24
0.844 12	0.015 56	298.47	21 094	21 143	78
1.001 97	0.020 52	298.19	20 656	20 662	40
1.201 44	0.016 94	298.07	20 251	20 238	49
1.500 58	0.018 43	298.22	19 728	19 737	35
1.701 43	0.020 40	298.25	19 652	19 667	68
2.002 04	0.020 72	298.25	19 020	19 033	18
2.009 83	0.017 29	298.24	19 046	19 057	85
2.502 32	0.019 99	298.31	18 351	18 370	69
3.002 16	0.020 17	298.25	17 531	17 542	37
3.502 12	0.018 20	297.95	17 029	17 009	50
4.001 55	0.018 21	298.07	16 406	16 398	23
4.501 78	0.018 53	298.07	15 803	15 797	36
5.001 76	0.015 82	298.07	15 472	15 467	47

The water used was doubly distilled, and the solid sample was Merck Suprapur. It was heated for 5 h in a furnace at 774 ± 5 K. The molalities are better than 0.01%, and the solute weighings are accurate to 0.003%.

Experimental Results

The measured differential enthalpies of solution of RbBr in water at 298.15 K are shown in Table I. The results were obtained by adding a small amount Δn_2 of solid salt to a solution of original molality m. Δm is the change of molality after the solution process, $\Delta_{sol}H_2^{exptl}(T)$ is the experimental differential enthalpy of solution at T, and $\Delta_{sol}H_2^{exptl}$(298.15 K) is the experimental differential enthalpy of solution adjusted to 298.15 K and after correcting for the error due to condensation of solvent vapor over the solution.

In Table I, ϵ is the estimated error in each calorimetric measurement. The values of ϵ were calculated from the uncertainties in the total energy change due to the noise in the base-line calorimeter.

0021-9568/89/1734-0182$01.50/0