**Registry No.** $N_2O$, 10024-97-2; $CO_2$, 124-38-9; glycerol, 56-81-5; 1,5-pentanediol, 111-29-5.

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**Supplementary Material Available:** Experimental raw data for absorption of both $CO_2$ and $N_2O$ into water, glycerol and 1,5-pentanediol aqueous solutions at 25 °C (4 pages). Ordering information is given on any masthead page.

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# Heats of Mixing of Binary Systems of *n*-Butylamine with Toluene and Methylcyclohexane at 288.15, 298.15, and 308.15 K

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**Heats of mixing of *n*-butylamine with toluene and with methylcyclohexane were measured at three temperatures in an isothermal dilution calorimeter. Experimental results were fitted with a Redlich–Kister polynomial. Both the experimental data and the Redlich–Kister coefficients for the smoothing of the data are reported.**

Recent studies of the quasi-chemical group approach to model liquid mixtures (*1*, *2*) have confirmed the importance of accurate heat-of-mixing data for the evaluation of group interaction parameters. A knowledge of the interactions of the amino group with other organic groups may be of potential use for the extension of group models to systems of interest in biochemical studies. Previous studies in our laboratory (*3*, *4*) have concentrated on binary systems containing amines with *n*-alkanes and *n*-alcohols. This work presents heats of mixing data for butylamine with toluene and with methylcyclohexane in an attempt to cover the interactions of the amine group with substituted aromatic and aliphatic rings. Measurements in this study were made at 288.15, 298.15, and 308.15 K.

## Materials and Apparatus

The materials used in this work were all supplied by Aldrich Chemical Co. with a stated purity of 99 mol %. The materials were used without further purification. Refractive indices of the chemicals, measured in a Bausch and Lomb refractometer, are compared with literature values in Table I.

**Table I. Refractive Indices of the Pure Compounds at 298.15 K**

| compound | refractive index: this work | refractive index: lit. value | ref |
|---|---|---|---|
| toluene | 1.4939 | 1.49405 | *6* |
| methylcyclohexane | 1.4210 | 1.4206 | *7* |
| *n*-butylamine | 1.3985 | 1.3991 | *8* |

**Table II. Experimental Heats of Mixing Values for the System *n*-Butylamine (1) + Toluene (2)**

| $x_1$ | $\Delta H$, J/mol | $x_1$ | $\Delta H$, J/mol | $x_1$ | $\Delta H$, J/mol |
|---|---|---|---|---|---|
| | | $T$ = 288.15 K | | | |
| 0.0449 | 117.4 | 0.4134 | 586.8 | 0.7594 | 411.7 |
| 0.1237 | 291.5 | 0.4581 | 592.1 | 0.8079 | 346.7 |
| 0.1587 | 352.6 | 0.5083 | 589.0 | 0.8634 | 261.2 |
| 0.2199 | 441.6 | 0.5459 | 582.2 | 0.8939 | 209.3 |
| 0.2730 | 502.8 | 0.5977 | 558.2 | 0.9266 | 149.9 |
| 0.3196 | 538.9 | 0.6432 | 527.9 | | |
| 0.3604 | 563.3 | 0.6965 | 480.9 | | |
| | | $T$ = 298.15 K | | | |
| 0.0429 | 104.4 | 0.4037 | 554.4 | 0.7588 | 392.6 |
| 0.0827 | 189.4 | 0.4481 | 564.8 | 0.8073 | 331.3 |
| 0.1530 | 316.8 | 0.5019 | 564.8 | 0.8626 | 249.8 |
| 0.2130 | 403.2 | 0.5576 | 552.6 | 0.9259 | 145.4 |
| 0.2652 | 462.0 | 0.6117 | 523.7 | 0.9610 | 79.3 |
| 0.3108 | 503.2 | 0.6595 | 490.4 | | |
| 0.3512 | 530.6 | 0.7156 | 439.8 | | |
| | | $T$ = 308.15 K | | | |
| 0.0411 | 93.3 | 0.4074 | 527.1 | 0.7827 | 350.7 |
| 0.0788 | 170.0 | 0.4495 | 535.6 | 0.8341 | 283.8 |
| 0.1470 | 288.1 | 0.5077 | 536.5 | 0.8624 | 241.0 |
| 0.2053 | 369.8 | 0.5581 | 523.6 | 0.9260 | 138.9 |
| 0.2561 | 427.9 | 0.6120 | 500.2 | 0.9619 | 73.3 |
| 0.3007 | 467.4 | 0.6776 | 457.0 | | |
| 0.3584 | 506.0 | 0.7159 | 421.9 | | |

The heats of mixing measurements were made in an isothermal semicontinuous dilution calorimeter of Van Ness type described in detail previously (*3*). In this work, the calorimeter was used in its endothermic mode of operation and perfluoroelastometer O-rings were used for the work with amine (*4*). The performance of the calorimeter was checked periodically by measuring the system 1-pentanol + *n*-heptane at 298.15 K (*5*). Its accuracy is believed to be within 1%, judging by the

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**Table III. Experimental Heats of Mixing Values for the System *n*-Butylamine (1) + Methylcyclohexane (2)**

| $x_1$ | $\Delta H$, J/mol | $x_1$ | $\Delta H$, J/mol | $x_1$ | $\Delta H$, J/mol |
|---|---|---|---|---|---|
| | | $T$ = 288.15 | | | |
| 0.0504 | 283.7 | 0.3909 | 1129.9 | 0.7490 | 760.2 |
| 0.0963 | 497.8 | 0.4452 | 1141.4 | 0.8099 | 607.0 |
| 0.1379 | 658.3 | 0.5043 | 1125.6 | 0.8563 | 481.1 |
| 0.1757 | 779.9 | 0.5549 | 1082.9 | 0.9086 | 320.0 |
| 0.2423 | 948.2 | 0.5991 | 1026.6 | 0.9675 | 119.1 |
| 0.2992 | 1046.2 | 0.6511 | 954.6 | | |
| 0.3481 | 1101.8 | 0.6966 | 872.1 | | |
| | | $T$ = 298.15 K | | | |
| 0.0506 | 281.2 | 0.3991 | 1106.5 | 0.7998 | 629.5 |
| 0.0942 | 474.5 | 0.4495 | 1115.9 | 0.8417 | 517.0 |
| 0.1337 | 622.6 | 0.5050 | 1101.3 | 0.8886 | 377.9 |
| 0.2047 | 833.3 | 0.6036 | 1013.5 | 0.9408 | 207.9 |
| 0.2642 | 960.5 | 0.6531 | 939.8 | 0.9696 | 108.2 |
| 0.3156 | 1038.0 | 0.6958 | 864.1 | | |
| 0.3600 | 1082.9 | 0.7441 | 762.7 | | |
| | | $T$ = 308.15 K | | | |
| 0.0482 | 250.3 | 0.3963 | 1088.1 | 0.7447 | 756.2 |
| 0.0916 | 443.0 | 0.4474 | 1100.6 | 0.8001 | 622.7 |
| 0.1317 | 595.0 | 0.5037 | 1089.1 | 0.8419 | 510.1 |
| 0.2013 | 804.3 | 0.5490 | 1061.1 | 0.8886 | 373.5 |
| 0.2610 | 935.1 | 0.6084 | 1004.5 | 0.9700 | 107.8 |
| 0.3122 | 1015.7 | 0.6573 | 931.5 | | |
| 0.3569 | 1063.3 | 0.6970 | 856.3 | | |

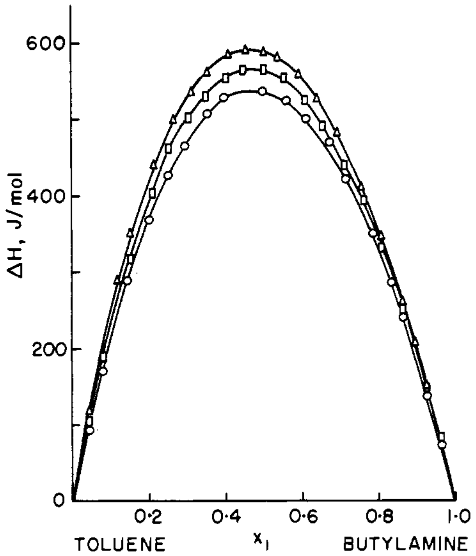

**Figure 1.** Heats of mixing for the system *n*-butylamine–toluene.

errors obtained in the repeated measurements of data for the system 1-pentanol + *n*-heptane at 298.15 K.

## Experimental Results

Experimental results for the system *n*-butylamine + methylcyclohexane at 288.15, 298.15, and 308.15 K are reported in Table II and for the system *n*-butylamine + toluene, at the same three temperatures, in Table III.

The data were fitted with a Redlich-Kister polynomial of the form

$$\Delta H = x_1x_2(A + B(x_1 - x_2) + C(x_1 - x_2)^2) \qquad (1)$$

Parameters for eq 1 are reported in Table IV for both binary systems at the three temperatures. The standard deviations of the fit are also reported in Table IV.

For reasons described below, the two last points of the butylamine-rich extreme of the composition range were left out of the fit for the system *n*-butylamine + methylcyclohexane at 298.15 K.

**Table IV. Parameters for Eq 1 (J/mol)**

| | *n*-butylamine + toluene | | | *n*-butylamine + methylcyclohexane | | |
|---|---|---|---|---|---|---|
| $T$, K | 288.15 | 298.15 | 308.15 | 288.15 | 298.15 | 308.15 |
| $A$ | 2366.7 | 2251.7 | 2146.1 | 4486.2 | 4393.6 | 4364.1 |
| $B$ | −299.8 | −232.7 | −187.3 | −1141.4 | −1072.3 | −938.8 |
| $C$ | 132.2 | 79.0 | 48.2 | 452.2 | 449.8 | 264.4 |
| std dev | 1.72 | 1.38 | 0.74 | 3.61 | 6.71 | 4.41 |

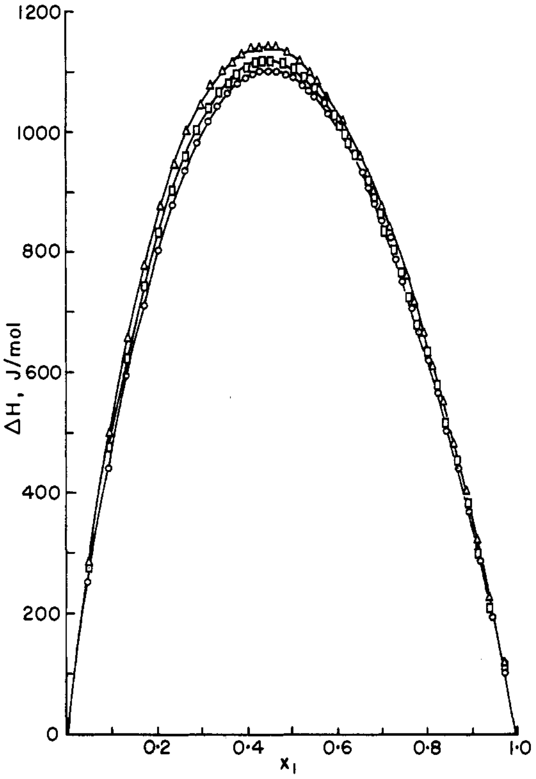

**Figure 2.** Heats of mixing for the system *n*-butylamine–methylcyclohexane.

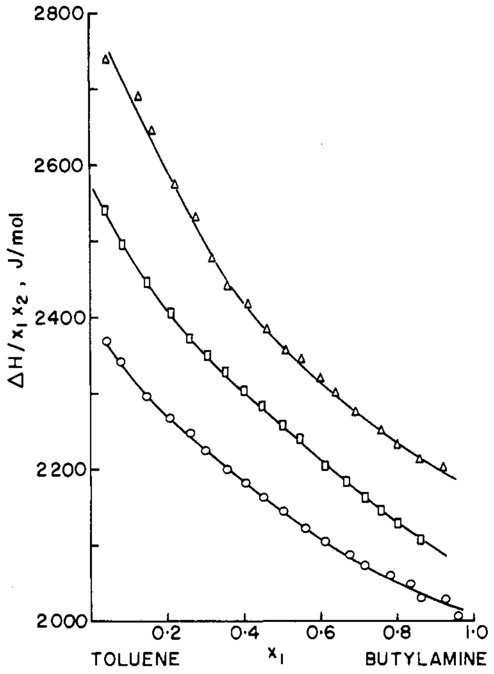

**Figure 3.** Values of $\Delta H/x_1x_2$ for the system *n*-butylamine–toluene.

## Discussion

Figure 1 depicts the heats of mixing for the system *n*-butylamine + toluene as a function of the mole fraction of *n*-butylamine at the three temperatures measured in this work. Figure 2 depicts a similar representation for the system *n*-amylamine + methylcyclohexane.

As can be seen from Figure 2, for the system *n*-butylamine + methylcyclohexane the curves of the heats of mixing for the three temperatures virtually coincide at the *n*-butylamine-rich extreme of the composition range. A study of the more sensitive representation of $\Delta H/x_1x_2$ versus $x_2$ showed that the last three points of the *n*-butylamine-rich extreme of the composition range at 298.15 K crossed the curve corresponding to 308.15 K. Calculations showed that an error in the mole fraction of 0.0004 was enough to produce this effect. Since this magnitude of error in the mole fraction is well within the experimental error of our measurements, the last two points of the *n*-butylamine-rich extreme of the composition range were eliminated from the smoothing of the data at this temperature.

For the system *n*-butylamine + toluene, Figure 1 shows a larger separation of the curves at the three temperatures and the above problem was not encountered. Figure 3 presents the curves of $\Delta H/x_1x_2$ versus $x_2$ for this system.

### Glossary

| | |
|---|---|
| $A$, $B$, $C$ | coefficients of the Redlich-Kister polynomial, J/mol |
| $T$ | temperature, K |
| $x$ | mole fraction |
| $\Delta H$ | heat of mixing per mole of mixture, J/mol |

*Subscripts*

| | |
|---|---|
| 1 | *n*-butylamine |
| 2 | toluene or methylcyclohexane |

**Registry No.** *n*-Butylamine, 109-73-9; toluene, 108-88-3; methylcyclohexane, 108-87-2.

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# Viscosities of Some Binary Ethyl Acetate Mixtures at 313.15 K

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**Viscosity coefficient measurements at saturation pressure are reported for ethyl acetate + *o*-xylene, ethyl acetate + *p*-xylene, ethyl acetate + *p*-dioxane, and ethyl acetate + tetrahydrofuran over the entire range of composition at 313.15 K. The values of mixture viscosity have been calculated for different compositions by the application of the Katti and Chaudhri equation. It was found that the experimental viscosities are in reasonable agreement with the calculated viscosities and within the uncertainty limits of ±0.003 cP. The absolute magnitude of the probable error does not change much from system to system.**

## Introduction

In recent years there has been considerable advancement in the experimental investigation of the excess thermodynamic properties of liquid mixtures. A survey of the literature shows that very few attempts (*1*, *2*) have been made to study viscosities of binary liquid mixtures containing esters. Therefore it was thought worthwhile to study viscosities of binary solutions of esters in polar and nonpolar solvents. Hence in the present program the measurements of viscosities for binary liquid mixtures of ethyl acetate with *o*-xylene, *p*-xylene, *p*-dioxane, and tetrahydrofuran have been made at 313.15 K.

## Experimental Section

Ethyl acetate (BHD, AnalaR), *o*-xylene, *p*-xylene, *p*-dioxane, and tetrahydrofuran all (BDH, AnalaR) were purified as per procedure given by Riddick and Bunger (*3*). Xylenes were freed from thiophene by shaking with sulfuric acid; the samples so obtained were washed with water followed by subsequent washing with sodium hydroxide and distilled water, dried thoroughly over anhydrous calcium chloride, and fractionally distilled twice. *p*-Dioxane was first refluxed with sodium hydroxide and then with sodium till free from peroxide and finally fractionally distilled over sodium. Tetrahydrofuran was treated with anhydrous ferrous sulfate, refluxed with potassium hydroxide for several hours and finally distilled over sodium. All the chemicals were distilled before use. Further, the purity of these samples was tested by measuring their densities, viscosities, and refractive indices at 303.15 K, which compared well with the literature values (*3*, *4*, 7), Table I.

Table I. Physical Properties of Pure Components in the Present Work and in the Literature at 303.15 K

| component | density ($d$), g cm$^{-3}$ exptl | density ($d$), g cm$^{-3}$ lit.$^a$ | viscosity ($\eta$), cP exptl | viscosity ($\eta$), cP lit.$^a$ | refractive index ($n_D$) exptl | refractive index ($n_D$) lit.$^a$ |
|---|---|---|---|---|---|---|
| ethyl acetate | 0.8885 | 0.8885 | 0.403 | 0.400 | 1.3680 | 1.3673 |
| *o*-xylene | 0.8717 | 0.8716<br>0.8717$^b$ | 0.693 | 0.693 | 1.5004 | 1.5003 |
| *p*-xylene | 0.8527 | 0.8523 | 0.564 | 0.568<br>0.566$^b$ | 1.4908 | 1.4907 |
| *p*-dioxane | 1.0227 | 1.0223 | 1.086 | 1.087 | 1.4180 | 1.4180 |
| tetrahydrofuran | 0.8788 | 0.8790$^c$ | 0.438 | 0.438$^b$ | 1.4028 | 1.4028$^b$ |

$^a$ Reference *4*. $^b$ Reference *3*. $^c$ Reference *7*.

Kinematic viscosities of the pure liquids and mixtures at different concentrations were determined at 313.15 K by using an Ubbelohde viscometer (*5*). The viscometer was calibrated against water and benzene. The time of efflux of a constant volume of liquid through the capillary was measured with the help of a precalibrated RACER stop watch accurate to ±0.1 s. The viscometer was always kept in a vertical position in a water thermostat. The thermostat bath was controlled to within ±0.01 °C. Once the temperature was stabilized the flow times for mixtures at different concentrations were measured. Stabilization was considered to be achieved when at least 4-5

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