**Table II. Properties Used in the NIBS Predictions**

| component (i) | $\bar{V}_i$, cm$^3$/mol | $\delta_i$,[a] (cal/cm$^3$)$^{1/2}$ |
|---|---|---|
| *n*-hexane | 131.51 | 7.27 |
| *n*-heptane | 147.48 | 7.50 |
| *n*-octane | 163.46 | 7.54 |
| cyclohexane | 108.76 | 8.19 |
| cyclooctane | 134.88 | 8.51[b] |
| dibutyl ether | 170.41 | 7.76 |
| isooctane | 166.09 | 6.86 |
| methylcyclohexane | 128.32 | 7.83[c] |
| anthracene | 150.00[d] | 0.01049[e] |

[a] Unless otherwise noted, solubility parameters are taken from ref *9*. [b] Calculated from the calorimetric data from ref *10*. [c] Calculated from data in ref *11*. [d] Value from ref *7*. [e] Value of $a_A^{solid}$ from ref *7*.

be estimated from the Scatchard–Hildebrand solubility parameter model

$$\Delta\bar{G}_{BC}^{ex} = \phi_B^0\phi_C^0(X_B^0\bar{V}_B + X_C^0\bar{V}_C)(\delta_B - \delta_C)^2 \quad (5)$$

where $\delta_i$ refers to the solubility parameter of component i.

Comparisons between experimental and predicted anthracene solubilities are tabulated in the last three columns of Table I. Solvent properties used in the NIBS predictions are listed in Table II. In general, eq 3 and 4 are comparable with identical overall average deviations of 2.1% and are superior to eq 2 which has an overall average (rms) deviation of 5.5%. More importantly, deviations for eq 3 and 4 fall almost within the experimental uncertainty of 1%. This indicates that approximation of dibutyl ether + alkane $\Delta\bar{G}_{BC}^{ex}$ values via eq 5 introduces only a relatively small error in the NIBS predictions and makes possible the calculation of presumed solute–dibutyl ether association constants from future solubility measurements.

## Glossary

| | |
|---|---|
| $a_A^{solid}$ | activity of the solid solute, defined as the ratio of the fugacity of the solid to the fugacity of the pure subcooled liquid |
| $(\Delta\bar{G}_A^{ex})^*$ | partial molar Gibbs free energy of the solute (Raoult's law), extrapolated back to infinite dilution |
| $(\Delta\bar{G}_A^{fh})^*$ | partial molar Gibbs free energy of the solute (Flory–Huggins model), extrapolated back to infinite dilution |
| $\Delta\bar{G}_{BC}^{ex}$ | excess Gibbs free energy of the binary solvent mixture based on Raoult's law |
| $\Delta\bar{G}_{BC}^{fh}$ | excess Gibbs free energy of the binary solvent mixture based on Flory–Huggins model, calculated from $\Delta\bar{G}_{BC}^{ex}$ values as $\Delta\bar{G}_{BC}^{fh} = \Delta\bar{G}_{BC}^{ex} + RT[\ln (X_B^0\bar{V}_B + X_C^0\bar{V}_C) - X_B^0 \ln \bar{V}_B - X_C^0 \ln \bar{V}_C]$ |
| $\bar{V}_i$ | molar volume of component i |
| $X_B^0$, $X_C^0$ | mole fraction compositions of solvent mixture, calculated as if the solute were not present |
| $X_A^{sat}$ | mole fraction solubility of solute |
| $\phi_B^0$, $\phi_C^0$ | ideal volume fraction composition of the solvent mixture, calculated as if the solute were not present |
| $\phi_A^{sat}$ | ideal volume fraction solubility of solute |
| $\delta_i$ | solubility parameter of component i |
| rms deviation | $(100/N^{1/2})\{\sum^N [\ln (X_{calcd}^{sat}/X_{exptl}^{sat})]^2\}^{1/2}$, % |

**Registry No.** Anthracene, 120-12-7; dibutyl ether, 142-96-1; hexane, 110-54-3; cyclohexane, 110-82-7; heptane, 142-82-5; methylcyclohexane, 108-87-2; octane, 111-65-9; isooctane, 540-84-1; cyclooctane, 292-64-8.

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# Thermodynamic and Spectroscopic Properties of 2-Pyrrolidinones. 1. Excess Molar Volumes of 2-Pyrrolidinone + Dichloromethane, + Dimethyl Sulfoxide, + Acetone, + 2-Propanol, and + Water

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**Negative excess molar volumes were measured for the binary liquid mixtures of 2-pyrrolidinone with acetone, dimethyl sulfoxide, dichloromethane, 2-propanol, and water at 303.15 and 323.15 K over the entire composition range. The results are discussed in terms of the possible interactions between like and unlike molecules.**

## Introduction

As part of a study on thermodynamic and physical properties of binary liquid mixtures containing amide as one of the components, we report here the excess molar volumes for five 2-pyrrolidinone liquid mixtures. Excess molar volumes at 303.15 and 323.15 K have earlier been measured for *N*-methylmethanesulfinamide, *N*,*N*-dimethylmethanesulfinamide, *N*,*N*-dimethylbenzenesulfinamide, and dimethyl sulfoxide with the solvents carbon tetrachloride, 1,4-dioxane, and benzyl alcohol, and the molecular interactions in these systems have been discussed (*1*–*3*). The systems have been selected with a view to studying the molecular interactions occurring in binary mixtures of N-monosubstituted and N,N-disubstituted sulfinamides and related sulfoxides (e.g. dimethyl sulfoxide) as one compo-

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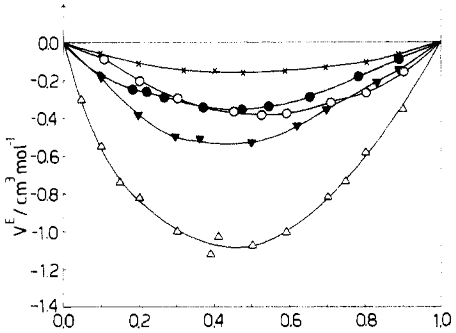


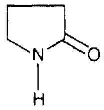
**Figure 1.** Excess molar volumes of 2-pyrrolidinone + dichloromethane (●), + dimethyl sulfoxide (×), + acetone (△), + 2-propanol (○), and + water (▼) at 303.15 K as a function of molar fraction ($x_1$) of 2-pyrrolidinone.

**Table I. Excess Molar Volumes ($V^E$) of 2-Pyrrolidinone–Solvent Mixtures at 303.15 K and 323.15 K**

| solvent | $x_1$ | $V^E$, cm$^3$ mol$^{-1}$ 303.15 K | $V^E$, cm$^3$ mol$^{-1}$ 323.15 K |
|---|---|---|---|
| dichloromethane | 0.0000 | 0.0000 | |
| | 0.0954 | −0.1703 | |
| | 0.1838 | −0.2523 | |
| | 0.2196 | −0.2638 | |
| | 0.2663 | −0.2930 | |
| | 0.3672 | −0.3480 | |
| | 0.4432 | −0.3579 | |
| | 0.4741 | −0.3572 | |
| | 0.5452 | −0.3412 | |
| | 0.6522 | −0.2956 | |
| | 0.7818 | −0.1860 | |
| | 0.8911 | −0.0982 | |
| | 0.9449 | −0.0514 | |
| | 1.0000 | 0.0000 | |
| dimethyl sulfoxide | 0.0000 | 0.0000 | 0.0000 |
| | 0.0980 | −0.0582 | −0.0691 |
| | 0.1985 | −0.1095 | −0.1238 |
| | 0.3182 | −0.1463 | −0.1728 |
| | 0.4013 | −0.1492 | −0.1894 |
| | 0.4757 | −0.1604 | −0.1892 |
| | 0.5866 | −0.1487 | −0.1913 |
| | 0.6956 | −0.1330 | −0.1692 |
| | 0.8031 | −0.1061 | −0.1291 |
| | 0.8870 | −0.0648 | −0.0801 |
| | 1.0000 | 0.0000 | 0.0000 |
| acetone | 0.0000 | 0.0000 | 0.0000 |
| | 0.0445 | −0.3031 | −0.3603 |
| | 0.1008 | −0.5490 | −0.7180 |
| | 0.1508 | −0.7376 | −0.8882 |
| | 0.2015 | −0.8263 | −1.0058 |
| | 0.3006 | −0.9983 | −1.2086 |
| | 0.3883 | −1.1180 | −1.3611 |
| | 0.4087 | −1.0291 | −1.2562 |
| | 0.4993 | −1.0727 | −1.2938 |
| | 0.5894 | −0.9971 | −1.2023 |
| | 0.7018 | −0.8170 | −0.9889 |
| | 0.7475 | −0.7352 | −0.8852 |
| | 0.8027 | −0.5853 | −0.7029 |
| | 0.9003 | −0.3553 | −0.4255 |
| | 1.0000 | 0.0000 | 0.0000 |
| 2-propanol | 0.0000 | 0.0000 | 0.0000 |
| | 0.1059 | −0.0911 | −0.1255 |
| | 0.2039 | −0.2074 | −0.2591 |
| | 0.3039 | −0.3001 | −0.3621 |
| | 0.4536 | −0.3704 | −0.4649 |
| | 0.5240 | −0.3903 | −0.4836 |
| | 0.5902 | −0.3831 | −0.4811 |
| | 0.7082 | −0.3243 | −0.3958 |
| | 0.8019 | −0.2725 | −0.3355 |
| | 0.9026 | −0.1659 | −0.2063 |
| | 1.0000 | 0.0000 | 0.0000 |
| water | 0.0000 | 0.0000 | 0.0000 |
| | 0.1006 | −0.1918 | −0.1382 |
| | 0.1986 | −0.3857 | −0.2978 |
| | 0.2940 | −0.5002 | −0.3960 |
| | 0.3600 | −0.5052 | −0.4258 |
| | 0.4975 | −0.5286 | −0.4291 |
| | 0.6185 | −0.4419 | −0.3640 |
| | 0.6984 | −0.3607 | −0.3015 |
| | 0.8308 | −0.2134 | −0.1741 |
| | 0.8877 | −0.1470 | −0.1204 |
| | 1.0000 | 0.0000 | 0.0000 |

nent and a moderately or weakly basic electron donor as the other.

2-Pyrrolidinone (I) is an interesting compound since it contains, in addition to the acidic NH proton, also a basic amidic carbonyl group. According to IR spectroscopic and dielectric measurements (*4–6*) the self-association of 2-pyrrolidinone is relatively strong and it was of interest to see whether some of the solvents can disturb the self-associated species through competition of their acidic or basic properties with those of 2-pyrrolidinone.



(I) 2-pyrrolidinone

## Experimental Section

2-Pyrrolidinone (purum, Fluka AG, Buchs, Switzerland) was purified by distillation above CaO and was preserved over molecular sieves 4A (*7*).

Dimethyl sulfoxide (purum, Fluka AG) was purified by distillation above $CaH_2$ and was preserved over molecular sieves 4A (*8*).

Acetone (p. a., E. Merck AG, Darmstadt, BRD) was refluxed 2 h with potassium permanganate, the solution was cooled, and $Na_2CO_3$ was added. Two hours later it was filtered and distilled and then dried and preserved over molecular sieves 4A (*7*).

2-Propanol (reinst, E. Merck AG) was purified by refluxing above CaO for 2 h and distilling. It was preserved over molecular sieves 4A (*7*).

Dichloromethane (p. a., E. Merck AG) was dried and preserved over molecular sieves 4A.

Water used was distilled and ion exchanged.

Densities were measured at 303.15 and 323.15 K with a digital density meter DMA 40 manufactured by Anton Paar K.G., Granz, Austria. Reproducibility of measurements was ±0.0001 g cm$^{-3}$. The density ($\rho$) of a liquid depends on the square of the period ($T$) of vibration of the sample tube according to the equation

$$\rho = A(T^2 - B) \tag{1}$$

where $A$ and $B$ are the calibration constants. Distilled water and air were used to obtain the constants.

## Results and Discussion

Excess molar volume data for the five binary 2-pyrrolidinone mixtures measured at 303.15 and 323.15 K are presented graphically in Figures 1 and 2. The experimental excess molar volume ($V^E$) was calculated by using the relation

$$V^E = \left(\frac{x_1M_1 + x_2M_2}{\rho_{12}}\right) - \left(\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2}\right) \tag{2}$$

where $x_1$ and $x_2$ are the mole fractions of 2-pyrrolidinone and the solvent, respectively, $M_1$ and $M_2$ are the molar masses of the components, and $\rho_1$, $\rho_2$, and $\rho_{12}$ are the densities of the

**Table II. Parameters of Eq 3 and the Standard Deviation $\sigma(V^E)$ for 2-Pyrrolidinone–Solvent Mixtures at 303.15 K and 323.15 K**

| solvent | $T$, K | $A_0$, cm$^3$ mol$^{-1}$ | $A_1$, cm$^3$ mol$^{-1}$ | $A_2$, cm$^3$ mol$^{-1}$ | $A_3$, cm$^3$ mol$^{-1}$ | $A_4$, cm$^3$ mol$^{-1}$ | $\sigma(V^E)$, cm$^3$ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|
| dichloromethane | 303.15 | −1.414 | −0.254 | 0.534 | −0.529 | −0.969 | 0.005 |
| dimethyl sulfoxide | 303.15 | −0.621 | −0.059 | −0.259 | 0.088 | 0.315 | 0.003 |
|  | 323.15 | −0.774 | −0.022 | −0.099 | 0.077 | 0.111 | 0.003 |
| acetone | 303.15 | −4.232 | −0.753 | −0.098 | −1.143 | −1.811 | 0.016 |
|  | 323.15 | −5.126 | −0.901 | −0.002 | −1.629 | −2.572 | 0.017 |
| 2-propanol | 303.15 | −1.540 | 0.120 | 0.212 | 0.703 | −0.049 | 0.005 |
|  | 323.15 | −1.923 | 0.207 | 0.604 | 0.641 | −0.773 | 0.008 |
| water | 303.15 | −2.066 | −0.873 | 0.047 | 0.602 | 0.564 | 0.011 |
|  | 323.15 | −1.704 | −0.702 | 0.123 | 0.702 | 0.654 | 0.004 |

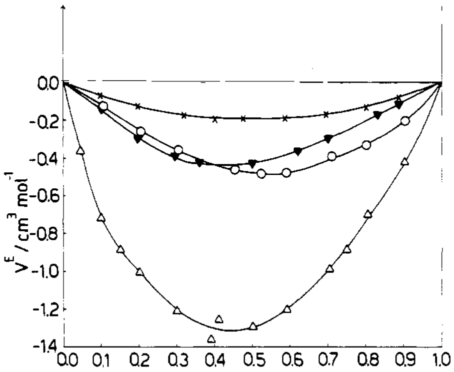


**Figure 2.** Excess molar volumes of 2-pyrrolidinone + dimethyl sulfoxide (×), + acetone (△), + 2-propanol (○), and + water (▼) at 323.15 K as a function of molar fraction ($x_1$) of 2-pyrrolidinone.

pure components and the mixture, respectively. The $V^E$ values together with the mole fractions for 2-pyrrolidinone + dimethyl sulfoxide, + acetone, + dichloromethane, + 2-propanol, and + water are given in Table I. Excess molar volumes are represented by the smoothing equation

$$V^E\ (\text{cm}^3\ \text{mol}^{-1}) = x_1(1 - x_1)\sum_{k=0}^{n} A_k(1 - 2x_1)^k \qquad (3)$$

where $k = 0, 1, ..., n$ and $x_1$ is the mole fraction of 2-pyrrolidinone. The parameters $A_k$ were evaluated by the method of least squares and are given in Table II along with the standard deviations. The standard deviation ($V^E$) was defined by

$$\sigma(V^E) = [\sum(V^E_{\text{obsd}} - V^E_{\text{calcd}})^2/(N - M)]^{1/2} \qquad (4)$$

where $N$ is the number of experimental points and $M$ is the number of parameters.

The $V^E$ data exhibited negative deviation in all studied systems, over the entire range of mole fraction and at both temperatures. The $V^E$ values in the systems 2-pyrrolidinone + 2-propanol and + water may be due to the dominance of the interaction between the carbonyl group of 2-pyrrolidinone and the OH group of 2-propanol or the water molecule over the other effects.

A rise in temperature leads to the breaking of hydrogen bonds and an increase in the fraction of unbonded molecules. The negative $V^E$ values at 303.15 and 323.15 K for 2-pyrrolidinone + water mixtures exhibit straightforwardly this trend, which suggests that the hydrogen bonds between water and carbonyl oxygen are stronger than those between water molecules, and hence the interaction between the unlike molecules gives a negative contribution to the $V^E$ values. Although the negative values for the excess quantities are indicative of relatively strong interactions between unlike molecules, the formation of complexes is nevertheless not unambiguously established from the thermodynamic data; 2-propanol, as an alcohol, and 2-pyrrolidinone, as a NH proton containing amide, for example, can self-associate by hydrogen bonding.

Further inspection of the data for the studied 2-pyrrolidinone mixtures shows the values of $V^E$ to decrease in the order dimethyl sulfoxide > dichloromethane > 2-propanol > water > acetone. Since the deviations from the ideality are smallest for dimethyl sulfoxide + 2-pyrrolidinone mixtures, the heteroassociation equilibria alone are not sufficient to account for the negative contribution to the $V^E$ values. The S=O bond in dimethyl sulfoxide is strongly polar and therefore the dielectric permittivity ($\epsilon$) and dipole moment ($\mu$) for dimethyl sulfoxide are high, 46.68 (at 298.15 K) and 13.0 × $10^{-30}$ C·m, respectively. The polarity contributes to making dimethyl sulfoxide a relatively basic compound, exceeding in basicity *N*-methyl-2-pyrrolidinone. The electron donor numbers (DN) are 29.8 for dimethyl sulfoxide and 27.3 for *N*-methyl-2-pyrrolidinone.

Positive deviation from ideality can be attributed to the changes in dipolar associations between the molecules. Since the dipole moments for amides and sulfoxides are very similar, it is unlikely that there will be any great differences in the dipolar contributions of dimethyl sulfoxide and 2-pyrrolidinone to the $V^E$ values of mixtures. Dissociation of self-associated species of 2-pyrrolidinone by dimethyl sulfoxide and/or a slight decrease in dipolar association of dimethyl sulfoxide may explain the small negative $V^E$ values for dimethyl sulfoxide + 2-pyrrolidinone mixtures compared with those for acetone + 2-pyrrolidinone mixtures. For both, the present study and earlier IR spectroscopic studies for the dimethyl sulfoxide + 2-pyrrolidinone pair suggest that the effect of weak hydrogen-bonded interaction between unlike molecules exceeds the effects of other factors in these binary mixtures.

The large negative deviation for acetone + 2-pyrrolidinone mixtures was expected, since the same behavior had been observed for acetone + *N*-methylacetamide mixtures (*9*). Both these amides can self-associate by hydrogen bonding, and the oxygen atom of acetone is a much weaker electron donor than that in dimethyl sulfoxide or in the carboxamide group.

Finally, the negative $V^E$ values for dichloromethane + 2-pyrrolidinone mixtures at 303.15 K suggest that the structure-making effects by charge-transfer complex formation between the unlike components exceed the structure-breaking effects in these binary mixtures. We earlier found the $V^E$ value to be negative for sulfinamide + carbon tetrachloride mixtures too.

**Registry No.** 2-Pyrrolidinone, 616-45-5; acetone, 67-64-1; dimethyl sulfoxide, 67-68-5; dichloromethane, 75-09-2; 2-propanol, 67-63-0; water, 7732-18-5.

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# Influence of Temperature on the Liquid–Liquid Equilibrium of the Ternary System Acetonitrile–2-Furyloxirane–Cyclohexane

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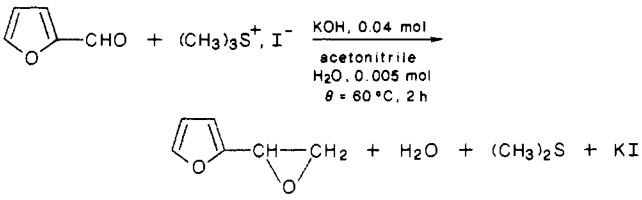
**2-Furyloxirane can be obtained by a low hydrated solid–liquid phase transfer process from furfural and a sulfonium salt in basic medium by using acetonitrile as a solvent. It is purified by extraction in a reactive medium with an extracting solvent, cyclohexane. Diagrams on solubility isotherms and tie-line data are given for the ternary system acetonitrile–2-furyloxirane–cyclohexane at 20–30 and 40 °C. Under these conditions 2-furyloxirane extraction by cyclohexane appears not to depend on temperature.**

## Introduction

2-Furyloxirane was synthesized from furfural in the presence of potassium hydroxide and trimethylsulfonium bromide.

Acetonitrile was used as a solvent and its hydration was rigorously quantified.

This reaction took place according to a solid–liquid transfer process (*1*, *2*). The reactive diagram is as follows:



Purification of 2-furyloxirane could not be achieved by distillation in reactive medium under atmospheric pressure. Indeed, the presence of water induced by the reaction caused an epoxide polymerization (*3*) at temperatures above 120 °C.

Intensive use of vacuum would not be rational for large-scale distillation.

Therefore extraction by solvent was necessary to separate this epoxide in the reaction medium and purify it.

Our work on the efficiency of various solvents led us to choose cyclohexane as the extracting solvent mainly because, at room temperature, it was partly miscible with acetonitrile and totally miscible with 2-furyloxirane.

## Experimental Section

***Chemicals.*** Trimethylsulfonium bromide was synthesized from dimethyl sulfide with a purity of 99% and methyl bromide cooled down to −30 °C. The reaction took place in acetonitrile for 10 h at room temperature. The initial concentration of reagents was 2 mol/L. The salt obtained was filtered and then dried under vacuum with a desiccator.

Potassium hydroxide powder was a commercial product with a minimum purity of 85%. Cyclohexane was a commercial product with a minimum purity of 99%. Commercial acetonitrile was dried with a 4 Å molecular sieve before use.

2-Furyloxirane was synthesized from furfural, potassium hydroxide, and trimethylsulfonium bromide in low hydrated acetonitrile according to a new method elaborated in our laboratory (*1*). At the end of the reaction, the reactive medium was filtered, concentrated in a vacuum, and then distilled at 30 °C under 1 Torr in order to obtain pure 2-furyloxirane with the following characteristics: bp = 56 °C (under 14 mmHg), $\alpha^{20}{}_{D}$ = 1.4845, and $D^{20}{}_{4}$ = 1.1411.

***Experimental Procedures.*** The solubility isotherms and the tie-line data for the ternary mixture acetonitrile–2-furyloxirane–cyclohexane were determined at various temperatures. Shaking as well as a constant temperature were maintained with a thermostated magnetic shaker. The mixing temperature was controlled by a mercury thermometer with ±0.5 °C accuracy.

Binaries of known compositions were prepared in order to determine the solubility binodal curves. On the left side of the slope (2-furyloxirane–acetonitrile) cyclohexane was added until the mixture became turbid. On the right side (2-furyloxirane–cyclohexane) acetonitrile was added until the mixture became turbid again. The contents of the three elements could then be determined by analysis.

Heterogeneous mixtures (acetonitrile–2-furyloxirane–cyclohexane) were prepared in order to determine the tie-line data. They were then shaken and left aside for 30 min to separate. Both equilibrium phases were separated and weighted. 2-Furyloxirane and acetonitrile were present in each phase and were measured with a chromatograph in gas phase (DEGS column 20%). Experimental conditions were as follows: length of column, 2.50 m; oven temperature, 180 °C; pressure of gas, 2.4 bar; internal standard, diethylbenzene; diluant solvent, diglyme.

We were able to check, thanks to data concerning both elements in each phase, that the conjugate points were actually on either side of the solubility isotherm.

***Solubility Point Error.*** The error introduced during the determination of titration end point in combination with the error in weighing permits one to obtain solubility points with relative accuracy of about 2 wt %.

***Tie-Line Error.*** The experimental error on the tie-line curve induced by several titrations (weighing, GPC) is estimated at about 2%.

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[‡] Laboratoire de Génie Chimique.

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