J. Chem. Eng. Data 1984, 29, 277-280

# Excess Gibbs Energy for Binary Mixtures Containing Carboxylic Acids. 1. Excess Gibbs Energy for Acetic Acid + Cyclohexane, + Benzene, and + *n*-Heptane

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**Vapor pressures of acetic acid + cyclohexane, + benzene, and + *n*-heptane at 298.15 and 318.15 K for the entire mole fraction range have been measured by a static method. Activity coefficients and excess Gibbs energies have been calculated from the data taking into consideration the dimerization of acetic acid in the vapor phase. All the systems show positive deviations from Raoult's law and mixtures with cyclohexane and *n*-heptane show maxima. Excess entropies have also been calculated and are very negative, indicative of the higher abundance of dimers with the increasing mole fraction of nonpolar solvent.**

## Introduction

Carboxylic acids are associated liquids having peculiar mixing behavior in various solvents (*1-7*). Mixtures of cyclohexane, benzene, and carbon tetrachloride—all nonpolar solvents—with acetic acid show large positive excess volumes. The acetic acid + carbon tetrachloride system has been reported by Kohler (*1*) to have $G^E$ 4-5 times larger than $H^E$, calling for a very negative excess entropy of mixing. This behavior is reported to have been caused by the increasing relative proportion of acid dimers with the increasing mole fraction of carbon tetrachloride.

Excess volumes of mixtures containing acetic, propionic, or isobutyric acid with a number of polar and nonpolar solvents have recently been reported (*5-7*) from our laboratories. In continuation of the measurement of the excess thermodynamic functions of such mixtures, we report in the present paper total vapor pressures of mixtures of acetic acid + cyclohexane, + benzene, and + *n*-heptane at 298.15 K and 318.15 K. Taking into consideration the dimerization of the acid in the vapor phase, we have calculated activity coefficients and excess Gibbs free energies of mixing.

## Experimental Section

***Purification of Chemicals.*** Glacial acetic acid (AR, BDH) was refluxed over phosphorus pentoxide and the fraction distilling at 118.2 °C was collected for the present work. Cyclohexane (LR, BDH) was made benzene free, and benzene (AR, BDH) thiophene free, by the procedures described elsewhere (*8*). Both these solvents and *n*-heptane (GR, Tokyo Kasei Kogyo Co., Ltd., Japan) were finally distilled over phosphorus pentoxide. The purities of chemicals were checked by determining their refractive indices and vapor pressures at 298.15 K, which have been compared with the literature values in Table I. The agreement is quite good.

***Method.*** The static manometric method was used to determine vapor pressures of mixtures. The details of the vacuum line consisting of two distillation assemblies for degassing the solvents, the Macleod gauge, measuring bulbs, the manometer, and the mixing cell appear elsewhere (*13*). The use of greased stopcocks was kept to a minimum by employing mercury cutoffs. The mixing cell was kept in a large-capacity water thermostat controlled to ±0.005 K. The temperature was measured with the help of a 0.001 K Beckmann thermometer. The manometer was housed in an air thermostat kept at 50 °C. The necessary correction to convert the pressure to 0 °C Hg was however employed. The Beckmann thermometer was calibrated by determining the transition temperature of Glauber's salt (32.384 °C). The pressures were read with a 0.001-cm cathetometer.

## Method of Calculations

The method used for the determination of activity coefficients of components from the total pressure and composition in the liquid phase is similar to the method reported by Kohler et al. (*1*). The vapor phase is considered to be an ideal mixture of acetic acid monomers, dimers, and solvent molecules. If we denote the amounts of monomers by $N_1$, the amounts of dimers by $N_2$, and the amounts of solvent by $N_B$, the stoichiometric amount of acetic acid in a given mixture, $N_A$, is given by

$$N_A = N_1 + 2N_2$$

and the dimerization constant $K_p$ in terms of partial pressures of the species becomes

$$K_p = (N_A - N_1)(N_A + N_1 + 2N_B)/(4PN_1^2)$$

The final activity coefficients of the two components involving their equilibrium are then given by

$$\ln \gamma_A = \ln (Py) - \ln (P_A{}^\circ x) - \ln (1 + S) + \ln [1 + (1 + 4K_pP_A{}^\circ)^{1/2}] \quad (1)$$

$$\ln \gamma_B = \ln \left[ \frac{P(1-y)}{P_B{}^\circ(1-x)} \right] + \ln \left[ \frac{1 + 4K_pP(2-y) - S}{2K_pP(2-y)^2} \right] \quad (2)$$

where

$$S = [1 + 4K_pPy(2-y)]^{1/2}$$

For the determination of $y$ and activity coefficients Kohler et al. (*1*) integrated the Gibbs-Duhem equation by the Runge and Kutta method selecting a suitable starting point. In the present evaluation the activity coefficients have been represented by the equations

$$\ln \gamma_A = Al_1 + Bm_1 + Cn_1 + Do_1 + Ep_1 + ... \quad (3)$$

$$\ln \gamma_B = Al_2 + Bm_2 + Cn_2 + Do_2 + Ep_2 + ... \quad (4)$$

where $A$, $B$, $C$, $D$, ... are constants and $l_1$, $m_1$, $n_1$, ... and $l_2$, $m_2$, $n_2$, ... are functions of mole fractions only (*14*), for which the expressions as obtained by solving eq 3 and 4 to satisfy the Gibbs-Duhem equation are given in the Glossary. Some trial values of $A$-$E$ were assumed, activity coefficients for all the mole fractions of a system studied were calculated, and at each mole fraction eq 1 and 2 were solved simultaneously for $P$ and $y$ by a numerical method. In this method trial $P$ was taken equal to experimental total pressure ($P_{\text{exptl}}$) and $y$ was calcu-

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Table I. Physical Constants of Pure Compounds

| | | refractive index at 298.15 K | | vapor press. at 298.15 K/torr | |
|---|---|---|---|---|---|
| index | compd | obsd | lit. | obsd | lit. |
| 1 | acetic acid | 1.3695 | 1.3699 (*8*) | 15.60 | 16.55 (*8*),[a] 15.70 (*9*) |
| 2 | cyclohexane | 1.4235 | 1.4235 (*8*) | 97.51 | 97.58 (*8*),[a] 97.23 (*10*) |
| 3 | benzene | 1.4979 | 1.4979 (*8*) | 95.01 | 95.13 (*8*),[a] 95.06 (*11*), 95.04 ± 0.03 (*12*) |
| 4 | *n*-heptane | 1.3857 | 1.3851 (*8*) | 45.15 | 45.72 (*8*),[a] 45.03 (*11*) |

[a] From Antoine's equation.

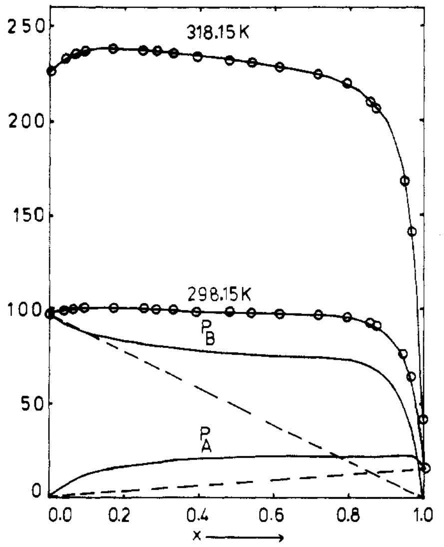

**Figure 1.** Plot of total pressure ($P$) and partial pressures ($P_A$, $P_B$) in torr against mole fraction ($x$) for acetic acid + cyclohexane system.

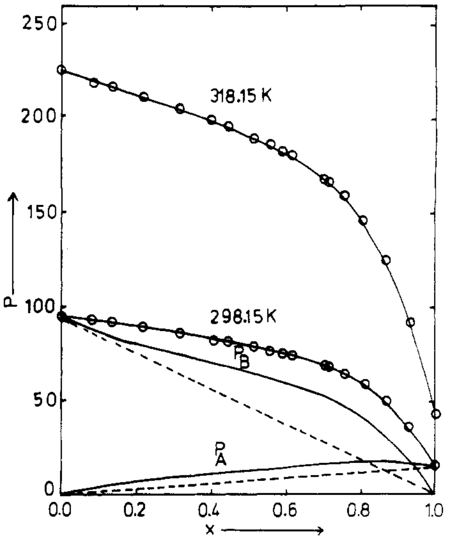

**Figure 2.** Plot of total pressure ($P$) and partial pressures ($P_A$, $P_B$) in torr against mole fraction ($x$) for acetic acid + benzene system.

lated from both eq 1 and 2. $P$ was changed until the difference between these two $y$ values ($\Delta y$) was less than $1 \times 10^{-5}$. The incremental step of $P$ was kept to $1 \times 10^{-3}$ torr. $P$ and $y$ corresponding to each mole fraction were thus determined. For minimizing the difference between the experimental and calculated pressures, called the residual pressure $P^R$, the dependence of $P$ upon $A$, $B$, $C$, ... was calculated from the following equations:

$$\partial P/\partial A = [l_1\gamma_A y + l_2\gamma_B(1 - y)]P = C_1$$

$$\partial P/\partial B = [m_1\gamma_A y + m_2\gamma_B(1 - y)]P = C_2$$

$$\partial P/\partial C = [n_1\gamma_A y + n_2\gamma_B(1 - y)]P = C_3$$

etc., and

$$P^R = (\partial P/\partial A)\,dA + (\partial P/\partial B)\,dB + ...$$

i.e.

$$P^R = C_1\,dA + C_2\,dB + ...$$

Using the least-squares method, we solved the following equations for $dA$, $dB$, $dC$, ...:

$$dA\,[\textstyle\sum(C_1)^2] + dB[\sum(C_1C_2)] + dC[\sum(C_1C_3)] + ... = C_1P^R$$

$$dA\,[\textstyle\sum(C_1C_2)] + dB\,[\sum(C_2)^2] + dC\,[\sum(C_2C_3)] + ... = C_2P^R$$

etc. Next trial values for $A$, $B$, $C$, ... thus become $A + dA$, $B + dB$, etc.

For each set of $A$, $B$, $C$, ... values the root mean square of residual pressures was calculated

$$\sigma = \left[\frac{\sum(P^R)^2}{\text{(no. of observations - no. of parameters)}}\right]^{1/2}$$

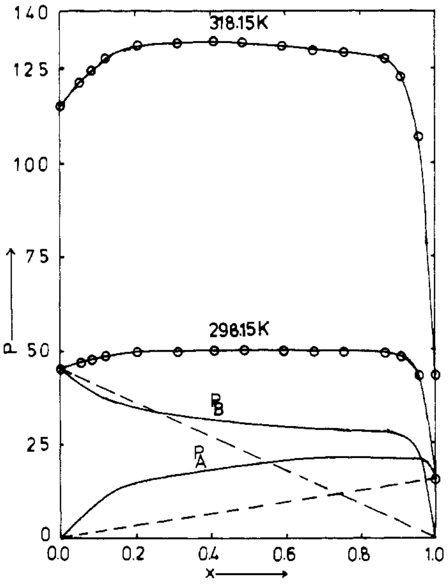

**Figure 3.** Plot of total pressure ($P$) and partial pressures ($P_A$, $P_B$) in torr against mole fraction ($x$) for acetic acid + $n$-heptane system.

and iterated until it became constant. For each final values are included in Table II. The computer calculations were done on a DEC System-20.

## Results and Discussion

Total vapor pressures as a function of composition for the three title systems measured at 298.15 and 318.15 K are given in Table II and the results at 298.15 K are illustrated in Figures 1-3 along with partial pressures. It is apparent that all the mixtures show positive deviations from ideal behavior and the mixtures with cyclohexane and $n$-heptane have maxima at

Table II. Vapor Pressures and Activity Coefficients for Acetic Acid + Solvent Systems at 298.15 and 318.15 K

| | 298.15 K | | | | | 318.15 K | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $x$ | $P$/torr | $\ln \gamma_A$ | $\ln \gamma_B$ | $y$ | $p^R$ | $P$/torr | $\ln \gamma_A$ | $\ln \gamma_B$ | $y$ | $p^R$ |
| | $CH_3COOH$ + c-$C_6H_{12}$ | | | | | $CH_3COOH$ + c-$C_6H_{12}$ | | | | |
| 0.0000 | 97.51 | 3.0723 | 0.0000 | 0.0000 | 0.00 | 225.85 | 3.1082 | 0.0000 | 0.0000 | 0.00 |
| 0.0405 | 99.09 | 2.4994 | 0.0113 | 0.0744 | 0.03 | 232.89 | 2.5195 | 0.0117 | 0.0909 | 0.31 |
| 0.0659 | 99.84 | 2.2199 | 0.0269 | 0.1065 | −0.08 | 234.95 | 2.2293 | 0.0279 | 0.1258 | −0.48 |
| 0.0961 | 100.41 | 1.9502 | 0.0505 | 0.1282 | 0.02 | 236.67 | 1.9470 | 0.0526 | 0.1471 | −0.24 |
| 0.1698 | 100.37 | 1.4950 | 0.1187 | 0.1563 | −0.20 | 237.55 | 1.4659 | 0.1247 | 0.1704 | −0.14 |
| 0.2457 | 99.64 | 1.2038 | 0.1941 | 0.1798 | −0.51 | 236.93 | 1.1589 | 0.2041 | 0.1898 | −0.19 |
| 0.2803 | 99.49 | 1.1023 | 0.2303 | 0.1901 | −0.31 | 236.27 | 1.0542 | 0.2415 | 0.1991 | −0.20 |
| 0.3276 | 99.21 | 0.9804 | 0.2835 | 0.2026 | −0.02 | 235.30 | 0.9312 | 0.2951 | 0.2115 | 0.03 |
| 0.3871 | 98.48 | 0.8429 | 0.3599 | 0.2145 | −0.02 | 233.81 | 0.7968 | 0.3698 | 0.2248 | 0.34 |
| 0.4744 | 98.35 | 0.6589 | 0.4994 | 0.2232 | 0.59 | 231.72 | 0.6219 | 0.5023 | 0.2380 | 0.75 |
| 0.5325 | 98.01 | 0.5462 | 0.6137 | 0.2247 | 0.42 | 230.26 | 0.5160 | 0.6097 | 0.2431 | 0.59 |
| 0.6081 | 97.64 | 0.4136 | 0.7900 | 0.2247 | 0.06 | 228.23 | 0.3909 | 0.7759 | 0.2476 | 0.04 |
| 0.7094 | 96.87 | 0.2631 | 1.0816 | 0.2272 | −0.18 | 224.39 | 0.2473 | 1.0543 | 0.2552 | −0.53 |
| 0.7875 | 95.42 | 0.1659 | 1.3724 | 0.2336 | 0.03 | 219.75 | 0.1542 | 1.3329 | 0.2659 | 0.47 |
| 0.8494 | 92.48 | 0.0986 | 1.6783 | 0.2434 | −0.04 | 210.14 | 0.0904 | 1.6225 | 0.2812 | −0.25 |
| 0.8644 | 91.46 | 0.0836 | 1.7679 | 0.2472 | 0.07 | 206.82 | 0.0764 | 1.7062 | 0.2868 | −0.20 |
| 0.9395 | 76.71 | 0.0214 | 2.3557 | 0.2986 | 0.03 | 169.75 | 0.0192 | 2.2456 | 0.3556 | 0.53 |
| 0.9618 | 64.52 | 0.0092 | 2.5908 | 0.3525 | 0.06 | 141.52 | 0.0082 | 2.4573 | 0.4200 | −0.23 |
| 1.0000 | 15.60 | 0.0000 | 3.0835 | 1.0000 | 0.00 | 43.35 | 0.0000 | 2.8956 | 1.0000 | 0.00 |
| | | | | | $\sigma$ = 0.29 | | | | | $\sigma$ = 0.45 |
| | $CH_3COOH$ + $C_6H_6$ | | | | | $CH_3COOH$ + $C_6H_6$ | | | | |
| 0.0000 | 95.01 | 2.0620 | 0.0000 | 0.0000 | 0.00 | 223.40 | 2.0731 | 0.0000 | 0.0000 | 0.00 |
| 0.0839 | 92.45 | 1.4451 | 0.0254 | 0.0451 | 0.60 | 218.61 | 1.4506 | 0.0257 | 0.0543 | 0.90 |
| 0.1331 | 91.08 | 1.1879 | 0.0565 | 0.0653 | 0.33 | 216.65 | 1.1912 | 0.0570 | 0.0772 | 0.98 |
| 0.2170 | 88.50 | 0.8719 | 0.1226 | 0.0903 | −0.43 | 211.67 | 0.8729 | 0.1235 | 0.1049 | −0.31 |
| 0.3146 | 86.30 | 0.6291 | 0.2094 | 0.1166 | −0.05 | 205.79 | 0.6292 | 0.2107 | 0.1338 | −0.63 |
| 0.4045 | 82.81 | 0.4707 | 0.2980 | 0.1418 | −0.54 | 199.19 | 0.4709 | 0.2992 | 0.1615 | −0.59 |
| 0.4431 | 81.95 | 0.4135 | 0.3400 | 0.1530 | 0.04 | 195.93 | 0.4139 | 0.3411 | 0.1737 | −0.62 |
| 0.5117 | 79.13 | 0.3220 | 0.4237 | 0.1728 | −0.05 | 189.88 | 0.3227 | 0.4244 | 0.1955 | −0.49 |
| 0.5550 | 76.97 | 0.2694 | 0.4838 | 0.1856 | −0.37 | 186.19 | 0.2703 | 0.4844 | 0.2094 | 0.02 |
| 0.5914 | 75.87 | 0.2279 | 0.5396 | 0.1965 | 0.18 | 182.50 | 0.2290 | 0.5399 | 0.2213 | 0.10 |
| 0.6191 | 74.85 | 0.1980 | 0.5854 | 0.2053 | 0.51 | 180.08 | 0.1992 | 0.5856 | 0.2307 | 0.76 |
| 0.7040 | 69.71 | 0.1170 | 0.7439 | 0.2368 | 0.34 | 168.17 | 0.1182 | 0.7741 | 0.2645 | 0.24 |
| 0.7128 | 68.38 | 0.1097 | 0.7618 | 0.2408 | −0.36 | 166.55 | 0.1108 | 0.7620 | 0.2687 | 0.06 |
| 0.7524 | 65.46 | 0.0792 | 0.8452 | 0.2614 | −0.05 | 159.10 | 0.0803 | 0.8457 | 0.2905 | 0.00 |
| 0.8049 | 59.69 | 0.0463 | 0.9610 | 0.2992 | −0.19 | 145.90 | 0.0471 | 0.9622 | 0.3302 | −0.30 |
| 0.8638 | 51.03 | 0.0202 | 1.0921 | 0.3686 | 0.08 | 125.28 | 0.0207 | 1.0950 | 0.4016 | −0.37 |
| 0.9295 | 36.66 | 0.0044 | 1.2273 | 0.5236 | 0.05 | 92.91 | 0.0045 | 1.2344 | 0.5568 | 0.46 |
| 1.0000 | 15.60 | 0.0000 | 1.3364 | 1.0000 | 0.00 | 43.35 | 0.0000 | 1.3477 | 1.0000 | 0.00 |
| | | | | | $\sigma$ = 0.37 | | | | | $\sigma$ = 0.60 |
| | $CH_3COOH$ + $n$-$C_7H_{16}$ | | | | | $CH_3COOH$ + $n$-$C_7H_{16}$ | | | | |
| 0.0000 | 45.15 | 2.4003 | 0.0000 | 0.0000 | 0.00 | 114.89 | 2.5000 | 0.0000 | 0.0000 | 0.00 |
| 0.0527 | 46.60 | 2.0645 | 0.0090 | 0.1142 | 0.13 | 121.19 | 2.1268 | 0.0099 | 0.1369 | 0.46 |
| 0.0847 | 47.81 | 1.8810 | 0.0225 | 0.1831 | 0.10 | 124.45 | 1.9270 | 0.0246 | 0.2088 | −0.31 |
| 0.1205 | 48.52 | 1.6937 | 0.0439 | 0.2369 | −0.25 | 127.53 | 1.7257 | 0.0476 | 0.2611 | −0.37 |
| 0.2061 | 49.53 | 1.3184 | 0.1165 | 0.3023 | −0.45 | 130.81 | 1.3298 | 0.1241 | 0.3196 | −0.40 |
| 0.3151 | 49.75 | 0.9691 | 0.2383 | 0.3388 | −0.62 | 131.85 | 0.9681 | 0.2502 | 0.3503 | −0.38 |
| 0.4110 | 49.98 | 0.7511 | 0.3619 | 0.3657 | −0.33 | 132.07 | 0.7438 | 0.3774 | 0.3736 | −0.14 |
| 0.4857 | 50.04 | 0.6191 | 0.4691 | 0.3879 | 0.00 | 131.96 | 0.6077 | 0.4878 | 0.3932 | 0.33 |
| 0.5906 | 49.84 | 0.4626 | 0.6520 | 0.4167 | 0.49 | 130.50 | 0.4470 | 0.6756 | 0.4185 | 0.43 |
| 0.6758 | 49.55 | 0.3440 | 0.8581 | 0.4309 | 0.73 | 129.48 | 0.3273 | 0.8834 | 0.4317 | 0.72 |
| 0.7528 | 49.43 | 0.2375 | 1.1265 | 0.4322 | 0.67 | 129.02 | 0.2227 | 1.1469 | 0.4351 | 0.72 |
| 0.8648 | 49.29 | 0.0926 | 1.7555 | 0.4230 | −0.20 | 127.52 | 0.0850 | 1.7433 | 0.4373 | −0.21 |
| 0.9076 | 48.28 | 0.0479 | 2.1054 | 0.4323 | −0.23 | 122.88 | 0.0436 | 2.0669 | 0.4546 | −0.42 |
| 0.9515 | 43.21 | 0.0147 | 2.5484 | 0.4889 | 0.58 | 106.89 | 0.0133 | 2.4713 | 0.5223 | −0.30 |
| 1.0000 | 15.60 | 0.0000 | 3.1569 | 1.0000 | 0.00 | 43.35 | 0.0000 | 3.0198 | 1.0000 | 0.00 |
| | | | | | $\sigma$ = 0.52 | | | | | $\sigma$ = 0.52 |

about $x$ = 0.16 and $x$ = 0.41, respectively. These maxima are more pronounced at higher temperatures (not shown). It may further be seen that these maxima are quite flat and continue right from $x \approx 0.1$ to $x \approx 0.9$. The maximum in the case of cyclohexane occurring around $x \approx 0.13$ and giving rise to an azeotrope boiling at 78.8 °C is well documented in the literature (*15*).

Activity coefficients of the components calculated from the measured vapor pressures using eq 1 and 2 are included in Table II. The values of the dimerization constant required at 298.15 and 318.15 K were calculated from the equation $\log K_p = -11.14 + 3410/T$ reported by Affsprung et al. (*2*) and are 1.9824 and 0.3786 $torr^{-1}$, respectively. The consistency of the activity data was checked by plotting $\ln \gamma_A/\gamma_B$ vs. $x$ and the area under the curves for each system was found to be negligible. The $A$, $B$, $C$, ... constants of eq 3 and 4 determined for various systems are summarized in Table III.

The excess Gibbs free energies calculated at rounded mole fractions at 298.15 K are given in Table IV and illustrated in Figure 4. The data at 318.15 K are similar except for increased magnitude. As the calculations of excess heats from the temperature dependence of the excess Gibbs free energies are highly discouraging (*1*), we have taken the values of excess heats measured at 298.15 K for acetic acid + cyclohexane and acetic acid + benzene systems in our laboratories (*16*) to calculate the $TS^E$ values (Table IV), which are very negative.

Table III. Values of Parameters of Eq 3 and 4

| $T$/K | $A$ | $B$ | $C$ | $D$ | $E$ |
|---|---|---|---|---|---|
| | | $CH_3COOH + c\text{-}C_6H_{12}$ | | | |
| 298.15 | 2.3116 | 0.1213 | 0.3631 | −0.1157 | 0.4032 |
| 318.15 | 2.2435 | 0.0535 | 0.4127 | −0.1596 | 0.3457 |
| | | $CH_3COOH + C_6H_6$ | | | |
| 298.15 | 1.4906 | −0.1432 | 0.2086 | −0.2196 | |
| 318.15 | 1.4936 | −0.1435 | 0.2168 | −0.2192 | |
| | | $CH_3COOH + n\text{-}C_7H_{16}$ | | | |
| 298.15 | 2.1750 | 0.2101 | 0.6036 | 0.1682 | |
| 318.15 | 2.1897 | 0.1472 | 0.5702 | 0.1127 | |

Table IV. $G^E$, $H^E$, and $TS^E$ Values (in J/mol) for Acetic Acid + Cyclohexane and Acetic Acid + Benzene Systems at 298.15 K

| | $CH_3COOH + c\text{-}C_6H_{12}$ | | | $CH_3COOH + C_6H_6$ | | |
|---|---|---|---|---|---|---|
| $x$ | $G^E$ | $H^E$ | $TS^E$ | $G^E$ | $H^E$ | $TS^E$ |
| 0.1 | 596.1 | 194.7 | −401.4 | 413.0 | 55.1 | −357.9 |
| 0.2 | 970.5 | 376.3 | −594.2 | 673.8 | 119.7 | −554.1 |
| 0.3 | 1217.6 | 537.0 | −680.6 | 830.5 | 178.6 | −651.9 |
| 0.4 | 1370.4 | 662.6 | −707.8 | 909.9 | 221.1 | −688.8 |
| 0.5 | 1432.6 | 736.2 | −696.4 | 923.9 | 240.5 | −683.4 |
| 0.6 | 1398.2 | 742.0 | −656.2 | 873.7 | 233.8 | −639.9 |
| 0.7 | 1260.4 | 668.7 | −591.7 | 756.1 | 201.7 | −554.4 |
| 0.8 | 1008.3 | 512.6 | −495.7 | 568.2 | 147.5 | −420.7 |
| 0.9 | 612.9 | 282.0 | −330.9 | 311.7 | 77.4 | −234.3 |

The same sign and similar magnitudes in the case of mixtures with $n$-heptane are expected. These negative entropies may be attributed to the predominant breaking of dimer–monomer interactions of acid molecules in favor of the formation of an increasing proportion of dimers with increasing mole fraction of the nonpolar component, in addition to dipole-induced dipole interactions. The present results are analogous to the results for acetic acid + carbon tetrachloride mixtures reported by Kohler et al. (*1*) leading to the conclusion of similar behavior for acetic acid in the title solvents.

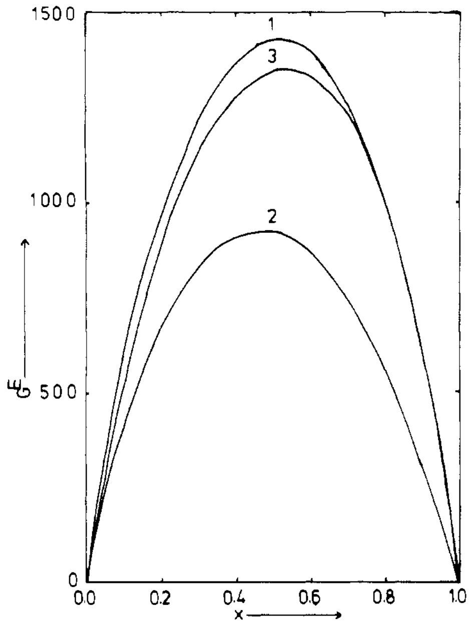

**Figure 4.** Plot of excess Gibbs free energy ($G^E$) in J/mol against mole fraction ($x$) at 298.15 K: (1) acetic acid + cyclohexane, (2) acetic acid + benzene, (3) acetic acid + $n$-heptane.

## Glossary

| | |
|---|---|
| $A$, $B$, $C$, ... | constants used in eq 3 and 4 |
| $\gamma_A$, $\gamma_B$ | activity coefficients of the acid and solvent |
| $G^E$ | excess Gibbs free energy of mixing |
| $H^E$ | excess enthalpy of mixing |
| $K_p$ | dimerization of acetic acid in vapor phase |
| $l_1$ | $=x_2^2$ |
| $m_1$ | $=-x_2^2(1 - 4x_1)$ |
| $n_1$ | $=x_2^2(1 - 8x_1 + 12x_1^2)$ |
| $o_1$ | $=-x_2^2(1 - 12x_1 + 36x_1^2 - 32x_1^3)$ |
| $p_1$ | $=x_2^2(1 - 16x_1 + 72x_1^2 - 128x_1^3 + 80x_1^4)$ |
| $l_2$ | $=x_1^2$ |
| $m_2$ | $=x_1^2(1 - 4x_2)$ |
| $n_2$ | $=x_1^2(1 - 8x_2 + 12x_2^2)$ |
| $o_2$ | $=x_1^2(1 - 12x_2 + 36x_2^2 - 32x_2^3)$ |
| $p_2$ | $=x_1^2(1 - 16x_2 + 72x_2^2 - 128x_2^3 + 80x_2^4)$ |
| $P$ | total pressure of the mixture |
| $P_A$, $P_B$ | partial pressure of acetic acid and solvent |
| $P_A^\circ$, $P_B^\circ$ | vapor pressure of pure acetic acid and pure solvent |
| $R$ | gas constant |
| $S^E$ | excess entropy of mixing |
| $T$ | temperature, K |
| $x$ | mole fraction of acid in liquid phase |
| $y$ | mole fraction of acid in vapor phase |

**Registry No.** Acetic acid, 64-19-7; cyclohexane, 110-82-7; benzene, 71-43-2; heptane, 142-82-5.

## Literature Cited

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Received for review July 18, 1983. Accepted November 14, 1983. T.S.B. is grateful to the CSIR, New Delhi, India, for the award of a junior research fellowship.