temperature. Table V collects the E_3 values (the relevant $E°$'s are to be found in Table IV) and Table VI the resulting pK_I values with the corresponding standard errors.

Conclusions

It must be emphasized that each pH_{RVS} value is valid only for the pH scale relevant to the specific (pure or mixed) solvent s considered (2, 7) and would be conveniently identified, e.g., by superscript s as ${}^{s}pH_{RVS}$. Values of ${}^{s}pH_{RVS}$ pertaining to different solvents would become physically comparable on an "intersolvental" pH scale with ultimate reference to the familiar pH scale in water (w) only by being preliminarily converted to ${}^{s}_{w}pH_{RVS}$ values by the equation (*2*)

$$ {}^{s}_{w}pH_{RVS} = {}^{s}pH_{RVs} + ({}^{w}E°_{H} - {}^{s}E°_{H})/k \qquad (15) $$

where ${}^{w}E°_{H}$ and ${}^{s}E°_{H}$ would be the absolute standard potentials (i.e., referred to a hypothetical electrode having standard potential invariant with varying solvent composition) of the hydrogen electrode in water and in the solvent mixture, respectively. The difference ${}^{w}E°_{H} - {}^{s}E°_{H}$ represents the so-called primary medium effect (*21*), is a measure of the Gibbs free energy of transfer of the H^+ ion from water to the solvent mixture, and, as such, is another extrathermodynamic quantity. An approach to its difficult quantification was recently made available (*22*).

Another interesting feature is that ${}^{s}pH_{RVS}$ is a continuous and smooth function of solvent composition and temperature, and sets of ${}^{s}pH_{RVS}$ data for an increasing number of aqueous mixtures with a variety of nonaqueous solvents can be processed together in terms of the above multilinear regression method to set up improved equations for *predicting* (*9*, *23*) reliable ${}^{s}pH_{RVS}$ values in still uninvestigated aqueous-organic solvent mixtures. The present data set provides an useful contribution also in such a context.

Registry No. *o*-Phthalic acid, 88-99-3; KH phthalate, 877-24-7.

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Solubility of Ethylene in *n*-Eicosane, *n*-Octacosane, and *n*-Hexatriacontane

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A semiflow gas absorption equilibrium apparatus is used to measure the solubility of ethylene in three paraffins (*n*-eicosane, *n*-octacosane, and *n*-hexatriacontane) at five pressures (10, 20, 30, 40, and 50 atm) and three temperatures (100, 200, and 300 °C).

Introduction

The three-phase slurry reactor has received much interest as being an effective reactor for the Fischer-Tropsch (F-T) synthesis (*1*). In this type of reactor the catalyst is suspended in a heavy molten wax and the synthesis gas is bubbled through the slurry. Several researchers (*2-4*) have found that the solubilities of the synthesis gases in the slurry were needed for interpretation of the reaction kinetics and for reactor design.

In this work we determined the solubility of ethylene, one of the F-T synthesis products, in three high molecular weight *n*-paraffins as model compounds of F-T wax: *n*-eicosane (n-C_{20}), *n*-octacosane (n-C_{28}), and *n*-hexatriacontane (n-C_{36}). A semiflow vapor-liquid equilibrium apparatus was used to obtain the data under F-T synthesis conditions, 100-300 °C and 10-50 atm.

Experimental Section

The semiflow solubility apparatus and operating procedure used in this work have been described by Huang et al. (*5*). Ethylene gas supplied from a cylinder is bubbled through a presaturator and an equilibrium cell in series while both are filled with a molten wax. The cells are contained in a thermostated nitrogen bath. After allowing sufficient time for equilibration, a

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Table I. Equilibrium Absorption of Ethylene in *n*-Eicosane

t, °C	P, atm	$x_{C_2H_4}$[a]
100.1	10.10	0.123
	20.06	0.228
	29.94	0.320
	40.04	0.395
	49.95	0.456
200.0	10.18	0.0820
	20.03	0.155
	29.91	0.221
	39.96	0.281
	49.91	0.335
300.0	10.12	0.0659
	20.06	0.132
	29.95	0.190
	39.98	0.245
	49.93	0.296

[a] Mole fraction of ethylene.

Table II. Equilibrium Absorption of Ethylene in *n*-Octacosane

t, °C	P, atm	$x_{C_2H_4}$[a]
99.9	10.04	0.147
	20.06	0.255
	30.02	0.344
	39.98	0.422
	49.94	0.488
199.9	10.03	0.0979
	20.00	0.181
	29.97	0.251
	39.99	0.311
	49.89	0.369
299.9	9.99	0.0804
	20.07	0.151
	30.01	0.214
	40.00	0.273
	49.98	0.321

[a] Mole fraction of ethylene.

Table III. Equilibrium Absorption of Ethylene in *n*-Hexatriacontane

t, °C	P, atm	$x_{C_2H_4}$[a]
100.1	10.13	0.172
	19.99	0.292
	29.97	0.393
	39.97	0.467
	49.93	0.527
199.9	10.09	0.113
	20.06	0.205
	29.95	0.280
	40.01	0.352
	49.97	0.403
300.1	10.10	0.0937
	20.07	0.177
	29.99	0.242
	39.97	0.306
	50.01	0.361

[a] Mole fraction of ethylene.

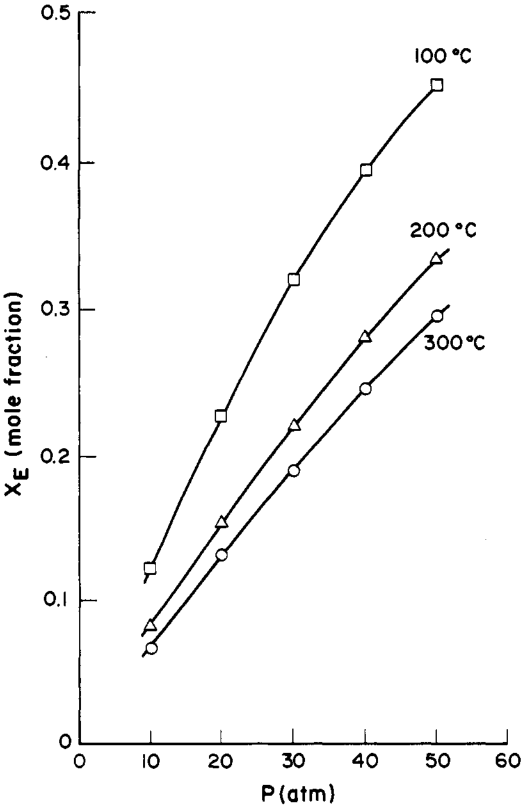

Figure 1. Solubility of ethylene in *n*-eicosane.

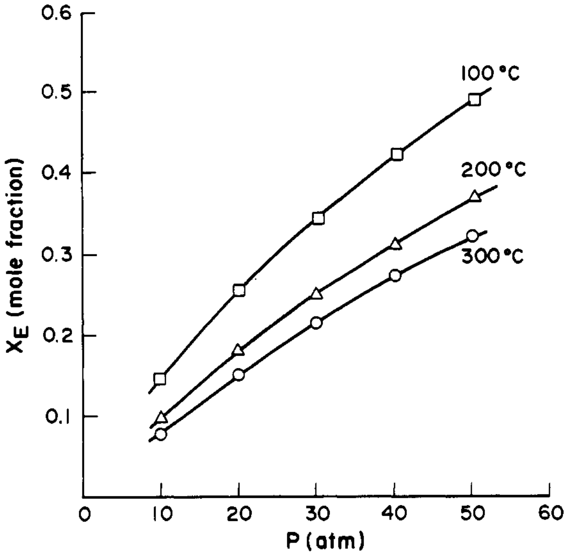

Figure 2. Solubility of ethylene in *n*-octacosane.

liquid sample is withdrawn from the bottom of the equilibrium cell into a liquid trap. Here the pressure is reduced, the liquid solidifies, and the gas from the sample passes into a buret where the volume is measured by water displacement. The mass of the wax sample is determined by difference from the preweighed trap. All temperatures of the apparatus are measured with type K Chromel–Alumel thermocouples accurate to within ±0.1 °C, and the pressure is measured with a Heise gauge with an accuracy of ±0.05 atm.

All three *n*-paraffins used in this work had a stated purity of 99%. *n*-Eicosane was purchased from Sigma Chemical Co., and *n*-octacosane and *n*-hexatriacontane were purchased from Aldrich Chemical Co. Gas chromatographic analysis showed no thermal degradation of the paraffins under experimental conditions. Ethylene was purchased from Matheson Gas Products with a stated purity of 99.5+%.

Results and Discussion

Tables I, II, and III present the equilibrium gas absorption data of this work for the absorption of ethylene in *n*-eicosane, *n*-octacosane, and *n*-hexatriacontane, respectively. The reported liquid-phase composition represents the average of three samples at a given temperature and pressure with the individual samples agreeing to within 1.5%.

Because of the low volatility of the *n*-paraffins at the conditions of this study, the vapor phase is essentially pure ethylene. The vapor composition was not measured. Calculations show the vapor is well over 99 mol % ethylene when absorbed

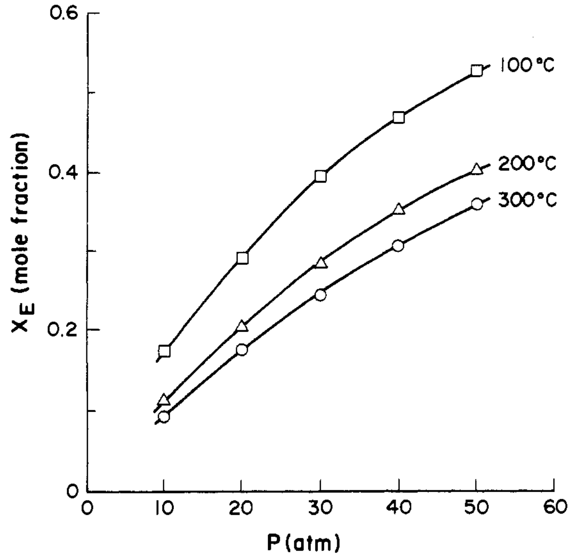

Figure 3. Solubility of ethylene in *n*-hexatriacontane.

in n-C_{28} and in n-C_{36} at all three temperatures of this study and when absorbed in n-C_{20} at 100 and 200 °C. However, when absorption is in n-C_{20} at 300 °C, there is an appreciable concentration of n-C_{20} in the vapor amounting to 0.04 mole fraction at 10 atm, 0.02 mole fraction at 20 and 30 atm, and 0.01 mole fraction at 40 and 50 atm. The calculation is based on ideal solution behavior for the paraffin in the liquid phase and the truncated two-term virial equation for the vapor. The second virial coefficient is estimated by the Pitzer correlation (*6*).

Figures 1-3 show the solubility isotherms of ethylene in the three paraffins studied. The solubility of ethylene in the *n*-paraffins decreases with increasing temperature. The amount of this decrease appears to decrease with increasing temperature; thus the drop in solubility from 100 to 200 °C is 2-3 times the decrease from 200 to 300 °C. Ethylene solubility increases with increasing pressure. The downward-bending curves of the isotherms indicate that this trend levels off slightly at higher pressures. It is also evident from the figures that at a given temperature and pressure the ethylene solubility expressed in mole fraction increases with increasing molecular weight of the solvent.

Registry No. n-C_{20}, 112-95-8; n-C_{28}, 630-02-4; n-C_{36}, 630-06-8; ethylene, 74-85-1.

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Solubility of Pyrene in Binary Solvent Mixtures Containing Dibutyl Ether

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Experimental solubilities are reported for pyrene in binary solvent mixtures containing dibutyl ether with *n*-hexane, cyclohexane, *n*-heptane, methylcyclohexane, *n*-octane, isooctane, and *tert*-butylcyclohexane at 26 °C. Results of these measurements, combined with estimates for the excess Gibbs free energies of the binary solvents, are used to test predictive expressions derived from the nearly ideal binary solvent (NIBS) model. Expressions based on a volume fraction average of solute properties in the two pure solvents predict pyrene solubilities to within a maximum deviation of 10% and an overall average deviation of 3.2%.

Introduction

This work continues a systematic study of solute solubility in binary solvent mixtures. Earlier papers have reported solubilities for iodine (*1*), benzil (*1*, *2*), *p*-benzoquinone (*3*), anthracene (*4*), benzoic acid (*5*), *p*-tolylacetic acid (*6*), pyrene (*7*), and carbazole (*8*-*10*). Benzil and *p*-benzoquinone solubilities in solvent mixtures containing carbon tetrachloride were particularly interesting as the mole fraction solubility covers a 14-fold and 6-fold range, respectively. The experimental data were interpreted with solution models developed previously for solubility in systems containing specific solute-solvent interactions and with models of purely nonspecific interactions. A stoichiometric complexation model based entirely on specific interactions (nonspecific interactions ignored) required several equilibrium constants to mathematically describe the experimental results, while the nearly ideal binary solvent (NIBS) model based on nonspecific interactions described adequately the observed solubilities without introducing a single equilibrium.

The success of the NIBS approach in predicting the binary solvent effect on benzil and *p*-benzoquinone solubilities suggested the possibility that this simple solution model may provide a foundation for approximations of physical interactions even in a system known to contain chemical interactions. To date, the NIBS model has been extended to systems containing a single solute-solvent association complex (*8*, *11*)

$$A + C \rightleftharpoons AC \qquad K_{AC} = \phi_{AC}/\phi_{A_1}\phi_{C_1}$$

$$\begin{aligned} \ln \phi_A^{sat} = {} & \phi_B{}^\circ \ln (\phi_A^{sat})_B + \phi_C{}^\circ \ln (\phi_A^{sat})_C + \\ & \ln [1 + K_{AC}\bar{V}_A\phi_C{}^\circ/(\bar{V}_A + \bar{V}_C)] - \phi_C{}^\circ \ln[1 + \\ & K_{AC}\bar{V}_A/(\bar{V}_A + \bar{V}_C)] + \frac{\bar{V}_A \Delta\bar{G}_{BC}^{fh}}{(X_B{}^\circ \bar{V}_B + X_C{}^\circ \bar{V}_C)RT} \end{aligned} \qquad (1)$$

and to systems in which the solute (component A) complexes with both solvents (components B and C) (*10*)

$$A + B \rightleftharpoons AB \qquad K_{AB} = \phi_{AB}/\phi_{A_1}\phi_{B_1}$$

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