value (*5*) of about 0.14 one would obtain if the 1*M* solubility alone were used to establish the slope. We can find no studies that report on the salting in and salting out of gases in the salt concentration range of 0 to 0.03*M*. Whether the high salting out constant of ethylene in this salt concentration range is due to some interaction of water, salt, and ethylene pi bonding system or the normal behavior of all gases in the limit of low salt concentration will require further study.

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Limiting Activity Coefficients of C_5 Hydrocarbons in Various Amides

HARRY M. SMILEY
Department of Chemistry, Eastern Kentucky University, Richmond, Ky. 40475

Gas-liquid chromatographic retention volumes and solute activity coefficients at infinite dilution have been determined for eight C_5 hydrocarbons in nine substituted amides. Temperature was varied so that partial heats of solution were obtained for the binary pairs involving solvents with relatively low vapor pressures at the indicated temperatures. Variation of activity coefficient with solvent structure is obvious.

ACTIVITY COEFFICIENTS determined by gas-liquid chromatography have appeared frequently in the literature recently and the experimental method is well known (*5*). The data produced in this manner are reproducible and are of interest from both a practical and a thermodynamic standpoint. In particular, one can get an idea of the relative nonideality of various binary pairs by this technique. Relative volatilities, obtainable from these data, are invaluable in solvent selection for extractive distillation precesses.

The following expression (*4*) relates the activity coefficient of the solute at infinite dilution in the liquid phase to the measured specific retention volume at 0° C.

$$\gamma_2^\infty = \frac{1.704 \times 10^7}{M p_2^\circ V_g^\circ} \tag{1}$$

where

γ_2^∞ = solute activity coefficient at infinite dilution
M = molecular weight of solvent
p_2° = vapor pressure of pure solute, mm. of Hg
V_g° = specific retention volume of solute, cc. of carrier gas per gram of solvent

Equation 1 assumes ideality of both the vapor phase above the solution and the pure solute vapor. The pure solute is chosen as the standard state; $\gamma_2 \rightarrow 1$ as $x_2 \rightarrow 1$ where x_2 is the solute mole fraction. The units of the constant in the numerator of Equation 1 are (cc.)(mm. of Hg).

For this work, a Beckman GC-2 chromatograph equipped with a thermal conductivity detector was used. A column packing was prepared, consisting of approximately 20% by weight of the liquid phase and 80% by weight of 60-mesh Johns-Manville Chromosorb W. The columns were 8-foot lengths of ¼-inch o.d. flexible copper tubing which could be easily coiled to fit the column chamber of the chromatograph. The carrier gas was helium and the flow was measured with a soap-film meter. The column outlet pressure was at all times atmospheric, and a mercury manometer to measure the inlet pressure was attached to a point immediately preceding the column inlet. Liquid hydrocarbon samples were injected with a 1.0-µl. Hamilton syringe. The solutes were obtained in pure form from the Phillips Petroleum Co. and blended before injection into the chromatograph. The solvents were used as received from the manufacturer. A reproducibility of values within 1% was realized for the activity coefficients.

To obtain the specific retention volumes, the following expression, developed by Littlewood (*3*), was employed:

$$V_g^\circ = \frac{(D)\ (F)}{(Z)\ (W)} \cdot \frac{273.2}{T_f} \cdot \frac{P_o - P_w}{P_o} \cdot 3/2 \cdot \frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \tag{2}$$

where

Table I. Solute Activity Coefficients at Infinite Dilution

	Solvent[a]								
	A	B	C	D	E	F	G	H	I
					At 24° C.				
n-Pentane	7.39	...	156	6.94	34.7	6.10	13.8	11.1	15.0
2-Methylbutane	7.07	...	129	6.70	32.7	5.91	13.6	10.6	14.2
2-Methyl-2-butene	4.86	...	57.4	4.62	17.7	3.59	6.28	5.55	6.86
3-Methyl-1-butene	5.08	...	63.3	4.84	18.7	3.97	6.94	6.15	7.91
1-Pentene	5.02	...	62.8	4.78	18.8	3.88	6.77	5.91	7.30
Isoprene	3.33	...	23.9	3.20	9.53	2.07	2.76	2.80	3.43
trans-Piperylene	3.46	...	25.4	3.34	9.82	2.06	2.76	2.81	3.49
cis-Piperylene	3.35	...	23.0	3.24	9.31	2.06	2.65	2.75	3.40
					At 40° C.				
n-Pentane	6.72	10.9	104	6.37	28.3	4.86	10.2	8.32	12.8
2-Methylbutane	6.44	10.5	104	6.18	30.3	4.77	9.66	8.05	12.5
2-Methyl-2-butene	4.49	6.65	43.2	4.30	14.9	2.88	4.90	4.18	6.11
3-Methyl-1-butene	4.54	6.86	50.2	4.45	15.8	3.10	5.47	4.91	6.74
1-Pentene	4.49	6.77	50.2	4.35	16.2	3.02	5.26	4.53	6.56
Isoprene	3.02	4.12	20.7	2.95	8.20	1.65	2.26	2.18	3.10
trans-Piperylene	3.09	4.22	21.5	2.99	8.32	1.64	2.25	2.19	3.06
cis-Piperylene	3.01	4.06	19.8	2.89	7.92	1.67	2.15	2.13	2.96
			At 70° C.				100° C., Solvent B		
n-Pentane	5.93	9.44	99.4	5.75	24.0		8.29		
2-Methylbutane	5.64	9.20	95.3	5.46	22.5		8.04		
2-Methyl-2-butene	4.10	5.98	35.3	3.96	12.8		5.31		
3-Methyl-1-butene	4.22	6.13	42.2	4.05	13.3		5.58		
1-Pentene	4.14	6.08	41.6	3.93	13.0		3.58		
Isoprene	2.92	3.88	16.9	2.77	7.22		3.58		
trans-Piperylene	2.97	3.95	17.6	2.86	7.25		3.51		
cis-Piperylene	2.89	3.83	16.2	2.78	7.04		3.68		

[a] A. *N*-Methylpropionamide. B. *N*-Methylacetamide. C. *N*-Methylmethane sulfonamide. D. *N*-Ethylacetamide. E. *N*-Methylformamide. F. *N,N*-Dimethylpropionamide. G. *N*-Methylpyrollidone. H. *N,N*-Dimethylacetamide. I. *N,N*-Dimethylformamide.

V_g° = specific retention volume of the solute
D = distance between air peak and solute peak, inches
Z = recorder chart speed, inches per minute
F = carrier gas flow rate, cc. per minute with soap-film meter
W = weight of liquid phase, grams
T_f = temperature of soap-film meter, ° K.
P_i = column inlet pressure, mm. of Hg
P_o = column outlet pressure, mm. of Hg
P_w = vapor pressure of water at T_f, mm. of Hg

Saturated vapor pressures of pure solutes were calculated by the Antoine equation:

$$\log p_2^\circ = A - \frac{B}{t + C} \tag{3}$$

where A, B, and C are the Antoine constants for the pure solute and t is the temperature in ° C. These Antoine constants are available in the literature (*1*) for most hydrocarbons through C_{20}.

RESULTS

The values of the limiting activity coefficients are listed at various temperatures in Table I. Some of these data are found elsewhere in the literature (*2*) and were intentionally included in this work as a check on experimental procedure. The activity coefficients published by Gerster (*2*) were not determined by a chromatographic technique, yet the agreement is reasonable.

During the experimental procedure, loss of liquid from the column was observed for certain solvents at higher temperatures: the *N,N*-disubstituted amides, but not the *N*-monosubstituted amides. This is due to lower vapor pressures of the latter solvents, and for these cases sufficient data were obtained to calculate the partial heats of solution. These partial heats of solution (listed in Table II) are obtained from the equation

$$\frac{d \log \gamma_2^\infty}{d\,(1/T)} = \frac{L_2}{2.303\,R} \tag{4}$$

Table II. Partial Heats of Solution (Cal./Mole) of C_5 Hydrocarbons with Various Solvents

	Solvent				
Solute	A	B	C	D	E
n-Pentane	960	1060	1830	815	1570
2-Methylbutane	990	1050	1270	901	1690
2-Methyl-2-butene	734	852	2070	665	1410
3-Methyl-1-butene	786	791	1730	1250	1450
1-Pentene	820	800	1760	843	1600
Isoprene	548	527	1510	613	1190
trans-Piperylene	631	704	1620	645	1300
cis-Piperylene	610	378	1540	633	1190

where L_2 is the partial heat of solution. Specifically L_2 is gotten from the integrated form of Equation 4 and is part of the slope of a straight line obtained from the plot of log γ_2^{∞} *vs.* $1/T$.

The magnitude of the activity coefficient of a given solute depends upon the solvent structure. Realizing that the activity coefficient values indicate the general trend that as the degree of nonideality of the hydrocarbon-solvent pair increases so does the magnitude of the activity coefficient, the following generalizations can be observed.

The nonideality of a binary pair involving a hydrocarbon and an *N*-monosubstituted amide of a given member of a homologous series is greater than the nonideality of a binary pair involving a hydrocarbon and an *N,N*-disubstituted amide of the same member.

The nonideality of a binary pair involving a given solute with successive members of the homologous series increases as the carbon number of the homologous series decreases.

The nonideality of a binary pair involving a given solute with a series of compounds varying only with the size of the *N*-substituted alkyl group increases as the carbon number of the *N*-substituted alkyl group decreases.

A greater degree of nonideality exists between a solute and a sulfonyl group than between the same solute and a carbonyl group.

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Physical Properties of Controlled-Solubility Phosphate Glasses

CHARLES W. LUTZ
Inorganic Chemical Research and Development Department, FMC Corp., Carteret, N. J. 07008

Viscosities, coefficients of expansion, and birefringence constants of several controlled-solubility phosphate glasses (sodium polyphosphates containing CaO, MgO, or Al_2O_3) were determined. For one of these glasses refractive index, intrinsic density, and crushing strength also were determined.

THE PROPERTIES of silicate glasses have been carefully determined and are readily available in the literature (*3*). The same is not true for the phosphate glasses. The usual commercial product is a rapidly dissolving linear sodium polyphosphate with an average of from six to 20 phosphorus atoms per chain. By substituting multivalent cation oxides—e.g., CaO, MgO, or Al_2O_3—for part of the Na_2O, series of useful controlled-solubility phosphate (CSP) glasses are obtained (*1*). Some physical properties of this type of glass were determined and are reported here.

EXPERIMENTAL RESULTS

Thermal properties were determined by the Emhart Glass Testing Laboratories, Hartford, Conn. The method used for coefficient of linear expansion (0° to 100° C) was ASTM C337-57; accuracy was estimated to be $\pm 3.0 \times 10^{-7}$ per °C, and was affected by glass solubility. Test errors that could result from glass solubility were minimized by making the tips blunt at the bearing ends of the 6-inch test piece. The sequence of "soaking" was from hot to cold to hot in each test. Any difference between the two hot-length readings was assumed to be a result of slow dissolving of glass at the tips. The difference was of the order of −0.00020 inch, a negligible error in the length of the 6-inch rod, but significant if the difference represented a ΔL change. A 0.00020-inch change in the ΔL produces an error of approximately 3.0×10^{-7} expansion unit. The second hot-bath reading was used in each case to determine the ΔL value. The other properties are defined in terms of log viscosity (in poises) and temperature (*3*). Annealing and strain points (ASTM C336-54T) and softening points (ASTM C338-57) were determined experimentally; the estimated accuracy for each temperature shown in Table I is ± 2° C. Flow point, working point, gob temperature, and melting temperature were obtained from the three experimentally determined viscosity points by an Emhart proprietary technique; these extrapolated temperatures are