

Table I: Densities of KOH Solutions

Temperature, °C.	Concn., Wt.% KOH	Number of Measurements	Density, G./Cc.
59.9	6.17	16	1.0381 ± 0.0001
	11.50	15	1.0863 ± 0.0002
	20.90	9	1.1758 ± 0.0002
	27.80	10	1.2448 ± 0.0001
	36.00	11	1.3294 ± 0.0002
	43.00	10	1.4080 ± 0.0001
	47.20	10	1.4560 ± 0.0001
79.9	50.37	10	1.4957 ± 0.0001
	6.17	9	1.0269 ± 0.0001
	11.50	10	1.0746 ± 0.0001
	20.90	9	1.1652 ± 0.0001
	27.80	10	1.2329 ± 0.0001
	36.00	10	1.3180 ± 0.0001
	43.00	10	1.3973 ± 0.0001
99.2	47.20	9	1.4442 ± 0.0008
	50.37	10	1.4848 ± 0.0001
	36.0	14	1.3073 ± 0.0001
	43.0	14	1.3858 ± 0.0001
	43.97	9	1.3969 ± 0.0001
	55.4	15	1.5324 ± 0.0001
	59.46	15	1.5809 ± 0.0001
120.5	55.4	20	1.5205 ± 0.0001
	59.46	18	1.5683 ± 0.0001
141	65.1	13	1.6342 ± 0.0001
	53.9	11	1.4901 ± 0.0001
	55.72	16	1.5160 ± 0.0001
	59.71	10	1.5622 ± 0.0001
161.4	65.1	10	1.6268 ± 0.0001
	64.68	16	1.6086 ± 0.0001
	72.25	16	1.7046 ± 0.0001
	77.1	16	1.7652 ± 0.0001

calculated by extrapolating values determined at lower temperatures using a power series in temperature for the volumetric expansion coefficient. Calibration of the plummet was repeated at frequent intervals during the measurements, and a small decrease in volume with time was observed at the higher temperatures. Solutions to be studied were maintained at the required temperature in an oil bath controlled to 0.02°C.

To prevent a rapid change in concentration by evaporation, an atmosphere of nitrogen presaturated with water vapor at a partial pressure equal to the equilibrium vapor pressure of the KOH solution was maintained over the surface of the sample studied. This was achieved by first passing the nitrogen stream through a series of presaturators containing pure water, and maintained at a temperature such that the vapor pressure of water was nearly equal to the known vapor pressure of the KOH solution (4) at the temperature under study. Final equilibration of the nitrogen stream was attained by passing it through a presaturator containing the KOH solution under study at the temperature of the density measurement. As a check against possible changes in concentration, a number of density measurements were made on the same sample and examined for any drift in density with time. At the higher temperatures, concentrations were determined by titration before and after an experiment.

RESULTS

The measured densities are shown in Table I. The uncertainties listed are the standard deviations from the arithmetic mean. The analysis accuracy was estimated to be 0.2% of the concentration value.

The data at 59.9° and 79.9°C. may be compared with hydrometer readings (4); agreement between the two sets of data is within 0.07% for almost all points.

LITERATURE CITED

- (1) Akerlof, G., Bender, P., *J. Am. Chem. Soc.* **63**, 1085 (1941).
- (2) Bauer, N., Lewin, S.Z., in "Technique of Organic Chemistry," Vol. 1, Part 1, A. Weissberger, Ed., Interscience, New York, 1959.
- (3) Kelly, W.R., Borza, P.F., Harriger, R.D., *J. CHEM. ENG. DATA* **10**, 233 (1965).
- (4) Solvay Process Division, Allied Chemical Corp., "Caustic Potash," *Solvay Tech. Eng. Serv. Bull.* No. 15, 1960.

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Vapor-Liquid Equilibria at 60°C. for *n*-Hexane-Alkyl Amines and 1-Hexene-Alkyl Amines

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EFFECTIVE separation of close boiling hydrocarbon mixtures often necessitates an uneconomical number of trays in a fractionator. An extractive distillation process may reduce the cost of the separation by changing the volatility characteristics of the mixture through the addition of a polar compound (solvent) to the hydrocarbon mixture. The solvent, if effective, will selectively interact with one or more of the hydrocarbon components. The solution complexities resulting from the interactions are difficult to define theoretically and quantitatively. This investigation is a por-

tion of an experimental program at The University of Texas to determine the influence of various types of polar compounds in modifying the solution nonideality.

Binary vapor-liquid equilibrium data were determined at 60°C. for *n*-butylamine, diethylamine, *n*-hexylamine, di-*n*-propylamine, diisopropylamine, and triethylamine with each of the hydrocarbons, *n*-hexane and 1-hexene.

EXPERIMENTAL

Materials. All materials used for the experimental work were checked for purity by a Beckman GC-2 gas chroma-

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Binary vapor-liquid equilibrium data are reported at 60° C. for *n*-butylamine, diethylamine, *n*-hexylamine, di-*n*-propylamine, diisopropylamine, and triethylamine with each of the hydrocarbons, *n*-hexane and 1-hexene. The *n*-butylamine was the most effective solvent in modifying the volatility of *n*-hexane relative to 1-hexene. The terminal binary hydrocarbon activity coefficient ratios produced by the various amines were: *n*-butylamine-1.23, *n*-hexylamine-1.18, diethylamine-1.14, di-*n*-propylamine-1.10, diisopropylamine-1.07, and triethylamine-1.03.

tograph, and a Bausch and Lomb precision refractometer. The normal boiling point was also used as an indication of the purity of the lower boiling materials. Table I summarizes the measured and reported values. Disagreement among some published literature values for the amines suggest that some properties, particularly refractive indices, have not been well established.

The two hydrocarbons used in this study, *n*-hexane and 1-hexene, were pure grade chemicals obtained from the Phillips Petroleum Co. The guaranteed minimum purities were 99 mole %, and, consequently, they were used without further purification.

The amines, supplied by the Union Carbide Chemicals Corp., were purified by chemical treatment and subsequent distillation. The liquid amines were in contact with potassium hydroxide pellets for a minimum of three days with intermittent agitation. The supernatant liquid was then drained off and distilled over reagent grade calcium oxide in a 35-plate Oldershaw column. The heartcut of the overhead product was used as the purified product. This procedure is similar to that used by Wiberg (12). The chromatograms of the purified materials indicated purities no lower than 99.3% after treatment.

The amines used in this study are members of either the C₄ or C₆ isomeric series and are primary, RNH₂, secondary, R₂NH, or tertiary, R₃N, where R is a saturated radical. These are listed below

Compound	Type	Structure
	C ₄ Series	
<i>n</i> -Butylamine	Primary	CH ₃ (CH ₂) ₃ NH ₂
Diethylamine	Secondary	(CH ₃ CH ₂) ₂ NH
	C ₆ Series	
<i>n</i> -Hexylamine	Primary	CH ₃ (CH ₂) ₅ NH ₂
Di- <i>n</i> -propylamine	Secondary	(CH ₃ CH ₂ CH ₂) ₂ NH
Diisopropylamine	Secondary	[(CH ₃) ₂ CH] ₂ NH
Triethylamine	Tertiary	(C ₂ H ₅) ₃ N

The principal difference between the normal primary and secondary amines in either series is chemical rather than physical, in that both compounds have identical molecular weights and similar structures but differ in the number of hydrogen atoms attached to the nitrogen atom.

Triethylamine is characterized by having no hydrogen atoms bonded to the nitrogen atom.

Apparatus and Procedure. The vapor-liquid equilibrium data (Table II) were obtained experimentally by use of a modified Colburn still. This apparatus has been previously described by Jones Schoeborn and Colburn (3).

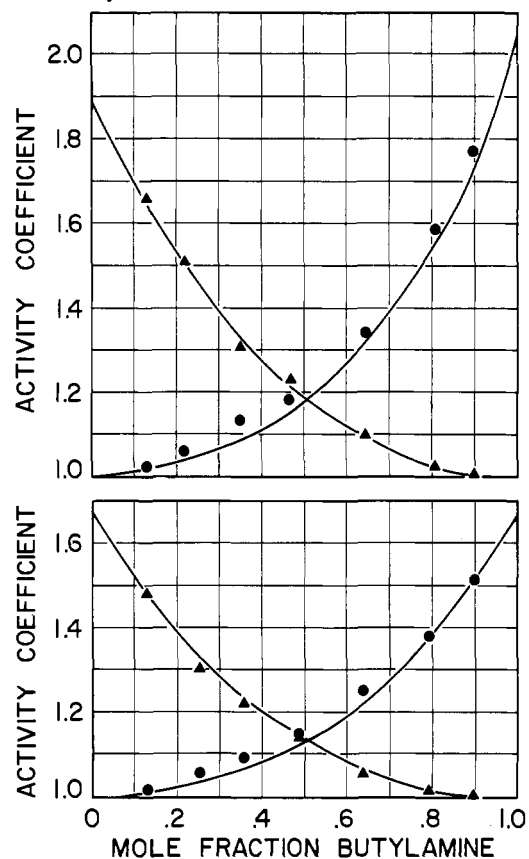


Figure 1. Variation of activity coefficient with composition at 60° C. for the *n*-butylamine and hydrocarbon systems

Top. *n*-Butylamine and *n*-hexane
Bottom. *n*-Butylamine and 1-hexene
Correlated by the Wilson equation

Table I. Comparison of Measured Properties with Literature Values

Compound	Molecular Weight	Normal Boiling Point		Refractive Index (<i>n</i> _D) at 20° C.	
		Experimental	Literature ^a	Experimental	Literature ^a
<i>n</i> -Hexane	86.2	68.78	68.74	1.37492	1.37486
1-Hexene	84.2	63.51	63.49	1.38792	1.38786
<i>n</i> -Butylamine	73.1	77.5	77.8	1.4009	1.40086
Diethylamine	73.1	55.33	55.5	1.38477	1.3850
<i>n</i> -Hexylamine	101.2	...	132.7	1.41842	1.4190
Di- <i>n</i> -propylamine	101.2	...	109.2	1.4040	1.4042
Diisopropylamine	101.2	83.3	83.5	1.39146	1.3912
Triethylamine	101.2	89.45	89.35	1.4013	1.4010

^a (1, 2, 9, 11).

Table II. Equilibrium Data at 60° C.

<i>n</i> -Butylamine (1) and <i>n</i> -Hexane (2) $A_{12} = 0.7842, A_{21} = 0.6023$					Di- <i>n</i> -propylamine (1) and <i>n</i> -Hexane (2) $A_{12} = 0.760, A_{21} = 1.0774$				
x_1	y_1	<i>P</i> , Mm.	γ_1	γ_2	x_1	y_1	<i>P</i> , Mm.	γ_1	γ_2
0.128	0.149	601.8	1.659	1.023	0.114	0.036	526.1	1.159	1.002
0.218	0.226	615.7	1.509	1.060	0.222	0.073	483.0	1.109	1.011
0.348	0.311	617.2	1.306	1.134	0.379	0.138	419.8	1.074	1.029
0.465	0.399	605.0	1.229	1.183	0.528	0.216	359.1	1.036	1.058
0.642	0.520	572.7	1.100	1.340	0.702	0.353	284.1	1.016	1.100
0.806	0.664	524.0	1.027	1.586	0.847	0.552	215.8	1.007	1.133
0.896	0.784	483.5	1.008	1.770	0.918	0.710	180.4	1.003	1.141
<i>n</i> -Butylamine (1) and 1-Hexene (3) $A_{13} = 0.7593, A_{31} = 0.7572$					Di- <i>n</i> -propylamine (1) and 1-Hexene (3) $A_{13} = 1.1834, A_{31} = 0.7780$				
x_1	y_1	<i>P</i> , Mm.	γ_1	γ_3	x_1	y_1	<i>P</i> , Mm.	γ_1	γ_3
0.129	0.119	680.6	1.479	1.013	0.112	0.027	620.4	1.040	1.004
0.251	0.206	676.4	1.306	1.056	0.218	0.058	564.1	1.045	1.007
0.354	0.277	661.8	1.221	1.091	0.376	0.116	478.0	1.034	1.009
0.483	0.368	634.8	1.142	1.146	0.379	0.116	477.9	1.018	1.015
0.634	0.478	592.5	1.057	1.253	0.534	0.196	394.7	1.021	1.020
0.791	0.635	532.8	1.017	1.383	0.694	0.322	308.1	1.016	1.028
0.897	0.784	481.9	1.003	1.517	0.834	0.506	231.6	1.004	1.044
Diethylamine (1) and <i>n</i> -Hexane (2) $A_{12} = 0.8703, A_{21} = 0.8805$					Diisopropylamine (1) and <i>n</i> -Hexane (2) $A_{12} = 1.0247, A_{21} = 0.8821$				
x_1	y_1	<i>P</i> , Mm.	γ_1	γ_2	x_1	y_1	<i>P</i> , Mm.	γ_1	γ_2
0.114	0.192	632.2	1.218	1.002	0.118	0.083	550.6	1.077	1.001
0.218	0.329	678.5	1.172	1.008	0.208	0.148	533.3	1.057	1.005
0.351	0.467	732.2	1.110	1.037	0.351	0.256	506.6	1.033	1.019
0.499	0.600	781.7	1.066	1.074	0.491	0.379	478.1	1.034	1.025
0.657	0.727	823.2	1.032	1.123	0.647	0.526	442.4	1.010	1.048
0.807	0.845	857.4	1.014	1.178	0.801	0.705	405.0	1.005	1.062
0.898	0.915	873.0	1.004	1.243	0.908	0.850	378.4	1.001	1.088
Diethylamine (1) and 1-Hexene (3) $A_{13} = 0.8129, A_{31} = 1.0614$					Diisopropylamine (1) and <i>n</i> -Hexane (2) $A_{13} = 1.0879, A_{31} = 0.8875$				
x_1	y_1	<i>P</i> , Mm.	γ_1	γ_3	x_1	y_1	<i>P</i> , Mm.	γ_1	γ_3
0.108	0.148	713.5	1.120	1.000	0.099	0.056	648.2	1.021	1.001
0.217	0.276	744.2	1.078	1.008	0.195	0.117	617.9	1.024	1.002
0.347	0.412	777.7	1.049	1.024	0.344	0.219	571.2	1.010	1.009
0.510	0.569	812.8	1.028	1.042	0.505	0.351	518.5	1.009	1.010
0.656	0.701	838.0	1.013	1.061	0.654	0.499	470.1	1.006	1.016
0.805	0.831	861.6	1.005	1.085	0.806	0.685	418.6	1.001	1.020
0.901	0.913	877.0	1.003	1.118	0.898	0.821	387.7	1.001	1.023
<i>n</i> -Hexylamine (1) and <i>n</i> -Hexane (2) $A_{12} = 0.588, A_{21} = 0.9378$					Triethylamine (1) and <i>n</i> -Hexane (2) $A_{12} = 1.2166, A_{21} = 0.7742$				
x_1	y_1	<i>P</i> , Mm.	γ_1	γ_2	x_1	y_1	<i>P</i> , Mm.	γ_1	γ_2
0.123	0.022	518.8	1.546	1.013	0.052	0.028	559.6	1.032	1.002
0.232	0.041	473.8	1.378	1.040	0.104	0.058	544.8	1.019	1.002
0.375	0.069	414.7	1.258	1.091	0.192	0.111	520.7	1.024	1.003
0.563	0.115	335.2	1.130	1.207	0.348	0.220	477.1	1.025	1.004
0.656	0.147	287.6	1.073	1.271	0.512	0.351	433.6	1.014	1.017
0.808	0.246	201.7	1.032	1.420	0.623	0.457	400.5	1.004	1.021
0.906	0.412	132.3	1.018	1.486	0.799	0.668	349.0	1.003	1.022
<i>n</i> -Hexylamine (1) and 1-Hexene (3) $A_{13} = 0.8383, A_{31} = 0.8581$					Triethylamine (1) and 1-Hexene (3) $A_{13} = 1.2077, A_{31} = 0.8052$				
x_1	y_1	<i>P</i> , Mm.	γ_1	γ_3	x_1	y_1	<i>P</i> , Mm.	γ_1	γ_3
0.112	0.014	612.8	1.270	1.005	0.103	0.048	639.4	1.007	1.001
0.216	0.029	557.0	1.210	1.024	0.200	0.099	600.9	1.003	1.001
0.360	0.054	480.5	1.175	1.060	0.348	0.189	543.8	0.999	1.005
0.553	0.099	371.7	1.096	1.127	0.505	0.309	481.6	1.005	1.001
0.648	0.132	317.1	1.073	1.178	0.652	0.450	425.1	1.002	1.006
0.841	0.281	183.4	1.033	1.260	0.820	0.666	359.8	1.003	1.005
0.890	0.369	145.6	1.021	1.270	0.912	0.818	324.6	1.003	1.009

Equilibrium temperatures were measured with copper-constantan thermocouples and a Leeds and Northrup Type K-2 potentiometer. The maximum error due to temperature measurement was estimated to be $\pm 0.1^\circ\text{C}$. A mercury manometer was used to measure system pressure. The mercury heights were measured with a cathetometer and a local gravity and temperature correction were applied. The maximum error due to pressure measurement was no more than ± 0.5 mm. of Hg. A Beckman GC-2 gas chromatograph was used in conjunction with a Brown 1-mv. recorder to determine composition. The maximum error encountered using this combination is no more than ± 0.2 mole %.

The quantities directly measured using this apparatus and procedure were the total pressure (P), the liquid composition (x), vapor composition (y), and the temperature (60°C).

Calculation of the Activity Coefficient. Activity coefficients were calculated at each experimental composition point by Equation 1. This equation is valid only for vapor-liquid equilibria at low pressures. The interested reader may refer to Van Ness (10) for the detailed development.

$$\ln \gamma_i = \ln(y_i P / x_i P_i) + (B_{ii} - V_i^L) (P - P_i) / RT + P \delta_{ij} y_j^2 / RT \quad (1)$$

where

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \quad (2)$$

and

$$B_{ij} = (\bar{B} - y_i^2 B_{ii} - y_j^2 B_{jj}) / 2y_i y_j \quad (3)$$

where B is the mixture virial coefficient. Each of the quantities appearing in the first term on the right side of Equation 1 were measured experimentally.

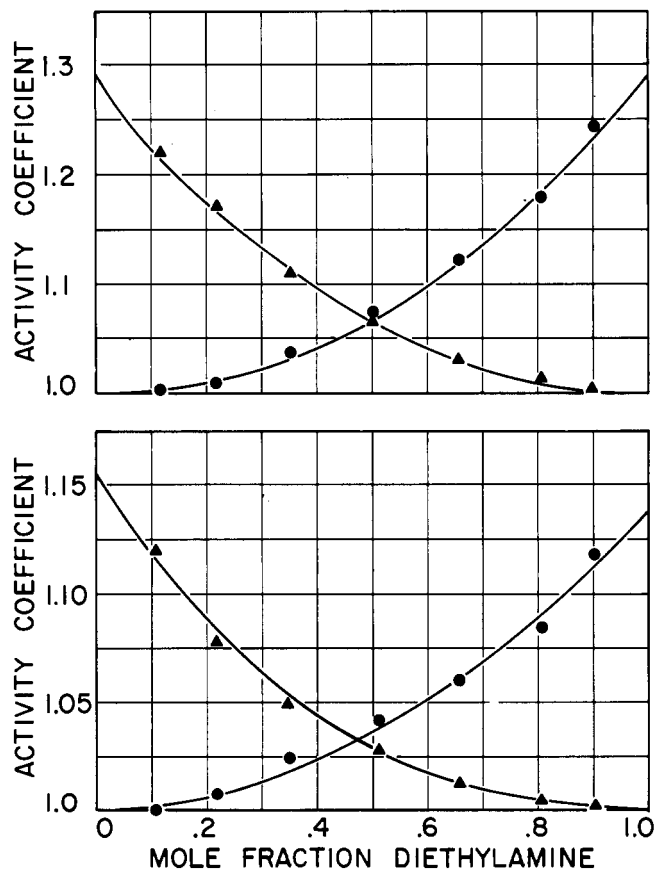


Figure 2. Variation of activity coefficient with composition at 60°C . for the diethylamine and hydrocarbon systems

Top. Diethylamine and *n*-hexane
Bottom. Diethylamine and 1-hexene
Correlated by the Wilson equation

Evaluation of the second term requires second virial coefficients for the pure components at the temperature of interest (60°C . in this case). Second virial coefficients for *n*-hexane and 1-hexene were determined using the correlation of McGlashan and Potter (6) and McGlashan and Wormold (7). Second virial coefficients for the amines were obtained from the data of Lambert (5) and by use of the Berthelot equation.

The largest contribution of the second term was about 6% (*n*-hexylamine-1-hexene system), and this term was included for all systems investigated.

The contribution of the third term on the right side of Equation 1 is most accurately determined if second virial coefficients for the mixture have been experimentally determined for the system at the temperature of interest. Unfortunately, such data are rarely available. To estimate the contribution of this term for the systems investigated, mixture second virial coefficient data for the cyclohexane-diethylamine system at 76°C . (4) were used to approximate the behavior of the *n*-hexane-diethylamine system at 60°C . The resulting calculation indicated a maximum contribution of about 0.8% to the activity coefficient. Other variables remaining equal, the contribution of the third term increases with total pressure. Fortunately, the diethylamine-hydrocarbon systems exhibited higher total pressures than the other systems studied and as a consequence of the small contribution in this higher pressure system, the third term was neglected for all systems investigated.

Correlation of Data. The Wilson equations have been tested for a number of systems by Orye and Prausnitz (8), and they were used in this investigation as a means to correlate

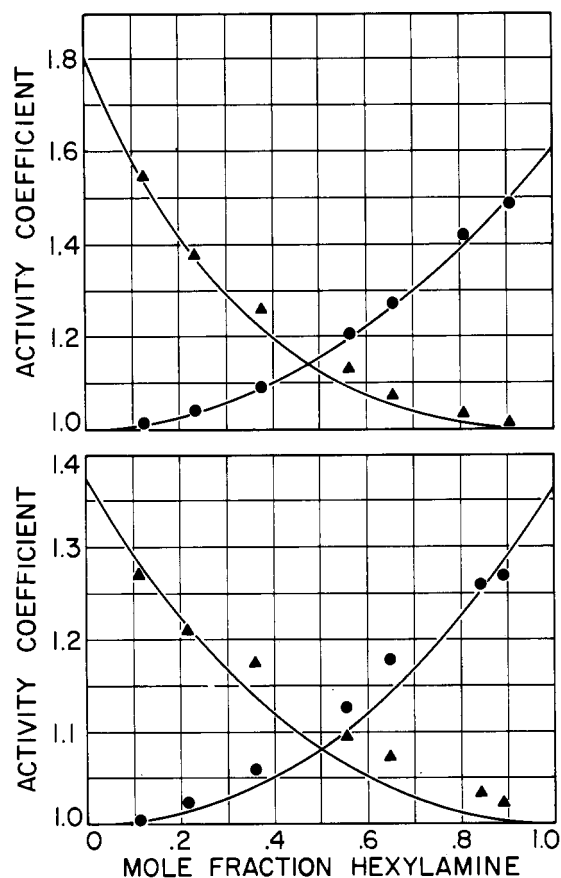


Figure 3. Variation of activity coefficient with composition at 60°C . for the *n*-hexylamine and hydrocarbon systems

Top. *n*-Hexylamine and *n*-hexane
Bottom. *n*-Hexylamine and 1-hexene
Correlated by the Wilson equation

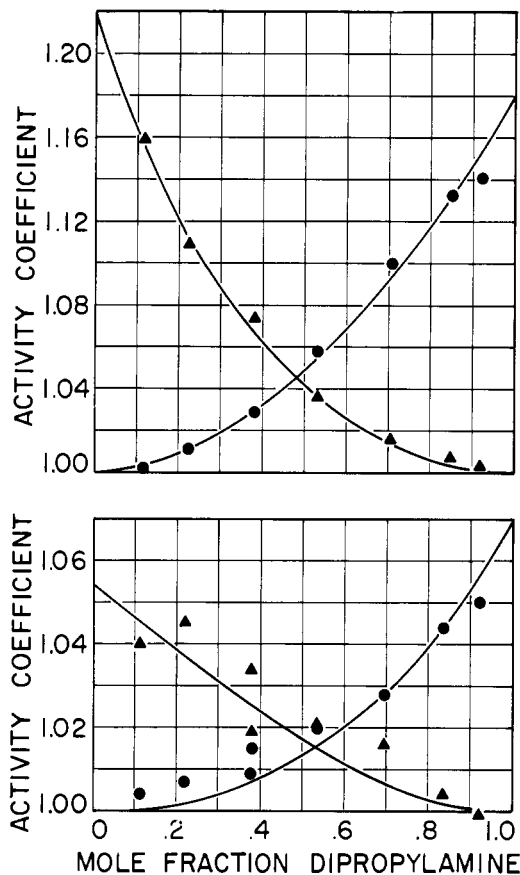


Figure 4. Variation of activity coefficient with composition at 60°C. for the di-*n*-propylamine and hydrocarbon systems
 Top. Di-*n*-propylamine and *n*-hexane
 Bottom. Di-*n*-propylamine and 1-hexene
 Correlated by the Wilson Equation

the activity coefficient data with composition. The Wilson equations for a binary system are:

$$\ln \gamma_i = -\ln(x_i + A_{ij}x_j) + x_j \left[\frac{A_{ij}}{x_i + A_{ij}x_j} - \frac{A_{ji}}{A_{ji}x_i + x_j} \right] \quad (4)$$

$$\ln \gamma_j = -\ln(x_i + A_{ji}x_j) - x_i \left[\frac{A_{ij}}{x_i + A_{ij}x_j} - \frac{A_{ji}}{A_{ji}x_i + x_j} \right] \quad (5)$$

at $x_i = 0$, Equation 4 becomes

$$\ln \gamma_i^\infty = -\ln A_{ij} + 1 - A_{ji} \quad (6)$$

while at $x_j = 0$, Equation 5 becomes

$$\ln \gamma_j^\infty = -\ln A_{ji} - A_{ij} + 1 \quad (7)$$

The parameters (A_{ij} and A_{ji}) were determined for each binary by inserting the corresponding activity coefficients at infinite dilution into Equations 6 and 7. The solution of the resulting equations necessitates a trial and error computation which is easily accomplished with a computer. The activity coefficients at infinite dilution, necessary for use in Equations 6 and 7, were obtained by extrapolating the function $\ln(\gamma_i/\gamma_j)$ to each respective composition end point. The ability of the Wilson equations to correlate the activity coefficient data is illustrated by the solid curves in Figures 1 through 6.

Calculation of Selectivity. An important parameter in the sizing of a distillation column is the relative volatility, which is defined as

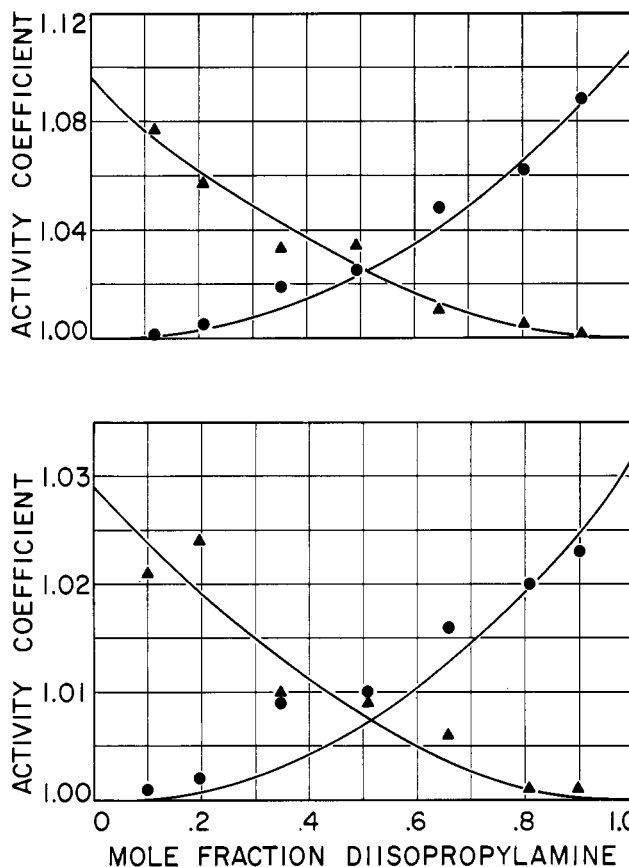


Figure 5. Variation of activity coefficient with composition at 60°C. for the diisopropylamine and hydrocarbon systems
 Top. Diisopropylamine and *n*-hexane
 Bottom. Diisopropylamine and 1-hexene
 Correlated by the Wilson equation

$$\alpha_{ij} = (y_i/x_i)/(y_j/x_j) \quad (8)$$

The liquid and vapor equilibrium compositions may, at moderate pressures, be related by combination of Raoult's and Dalton's laws. The result is:

$$y_i = P_i x_i \gamma_i / P \quad (9)$$

Direct use of Equations 8 and 9 yield

$$\alpha_{ij} = (P_i/P_j)(\gamma_i/\gamma_j) \quad (10)$$

The contribution of the change in the ratio P_i/P_j to the change in α_{ij} , which is due to addition of a solvent, is normally negligible compared with the contribution of the ratio γ_i/γ_j . As a result, the ratio γ_i/γ_j takes on a special significance and is defined as the selectivity.

$$S_{ij} = \gamma_i/\gamma_j \quad (11)$$

Equation 11 is applicable to the ternary composed of the hydrocarbons plus the solvent.

To form a relative comparison of solvent effectiveness from binary data alone, hydrocarbon activity coefficients were determined at the composition end point, where the concentration of solvent in each hydrocarbon-solvent binary approaches unity. Values determined in this manner are given the following symbolism.

$$S_{23}^\infty = \gamma_2^\infty/\gamma_3^\infty \quad (12)$$

where γ_2^∞ = activity coefficient of *n*-hexane(2) in the *n*-hexane-solvent binaries at $x_2 = 0$; and γ_3^∞ = activity coefficient of 1-hexene(3) in 1-hexene-solvent binaries at $x_3 = 0$.

The limiting selectivities so obtained are tabulated, for each amine, in Table III.

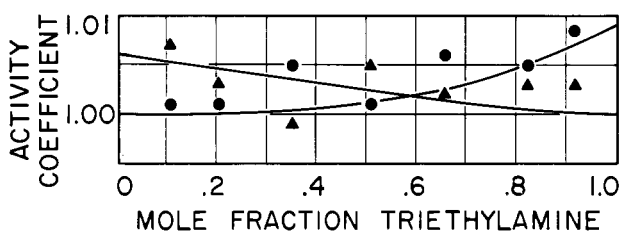
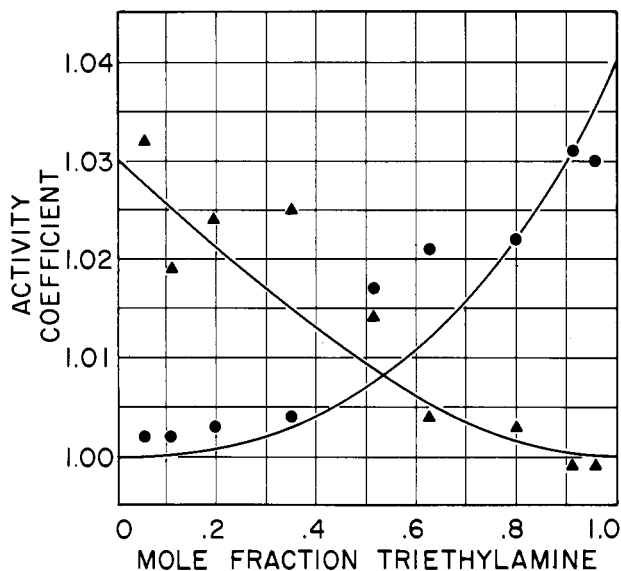


Figure 6. Variation of activity coefficient with composition at 60°C. for the triethylamine and hydrocarbon systems

Top. Triethylamine and *n*-hexane
Bottom. Triethylamine and 1-hexene
Correlated by the Wilson equation

Table III. Selectivities of *n*-Hexane (2) and 1-Hexene (3) at 60°C.

Solvent	S ₂₃
<i>n</i> -Butylamine	1.23
<i>n</i> -Hexylamine	1.18
Diethylamine	1.14
Di- <i>n</i> -propylamine	1.10
Diisopropylamine	1.07
Triethylamine	1.03

RESULTS AND CONCLUSIONS

Experimental data for each hydrocarbon and solvent binary indicate that the deviation from ideality increases in either isomeric solvent series as the number of nitrogen-bonded hydrogen atoms increases, or with respect to solvent type, in the order of tertiary, secondary, to primary amine. In addition, the deviation increases with decreasing molecular weight for the same type of amine. The largest deviations occur in the *n*-butylamine and *n*-hexane binary while the smallest values occur in the essentially ideal system, triethylamine and 1-hexene.

The selectivity values, tabulated in Table III, show that *n*-butylamine, containing the most nitrogen-bonded hydro-

gen atoms and smallest molecular size, is the most selective. Furthermore, for the same molecular size, the selectivity increases in the same order as it does for the deviation from ideality, tertiary, secondary, to primary amine, and for a given type of amine, such as primary, the selectivity increases with decrease in size. In particular, *n*-butylamine is more selective than diethylamine, yet they have identical molecular weights and similar molecular structures, the principal difference being in the number of hydrogen atoms bonded to the nitrogen atom. The same is true for the *n*-hexylamine and di-*n*-propylamine pair. Triethylamine, containing no nitrogen-bonded hydrogen atoms produces the lowest selectivity.

The difference in selectivities, taking the nature of the solvents into account, points to the formation of a complex between the nitrogen-bonded hydrogen atoms and the double bond of 1-hexene as the principal contributor to the selectivity mechanism for the amines and two hydrocarbons investigated here.

NOMENCLATURE

A_{ij}, A_{ji} = Wilson parameters
 B = mixture virial coefficient
 B_{ii} = virial coefficient of pure component i
 B_{ij} = interaction virial coefficient
 P = total system pressure
 P_i = vapor pressure of component i at the system temperature
 R = universal gas constant
 S_{23}^* = selectivity (ratio of γ_2^* to γ_3^*)
 T = absolute temperature
 V_i^L = liquid molar volume of pure component i
 x_i = mole fraction of component i in the liquid phase
 y_i = mole fraction of component i in the vapor phase

Greek

α_{ij} = volatility of hydrocarbon i relative to j
 γ_i = liquid phase activity coefficient for pure component i
 γ_i^* = liquid phase activity coefficient of component i at $x_i = 0$
 δ_{ij} = special virial function

Subscripts

1 = solvent (amine)
 2 = *n*-hexane
 3 = 1-hexene

LITERATURE CITED

- (1) "Beilsteins' Handbuch Der Organischen Chemie," 4th ed., Springer-Verlag, Berlin, 1955.
- (2) Dreisbach, R.R., *Advan. Chem. Ser.* **29**, 288 (1961).
- (3) Jones, C.A., Schoeborn, E.M., Colburn, A.P., *Ind. Eng. Chem.* **35**, 666 (1943).
- (4) Lambert, J.D., Murphy, S.J., Sanday, A.P., *Proc. Roy. Soc. (London)* **A226**, 394 (1954).
- (5) Lambert, J.D., Strong, E.D.T., *Ibid.*, **A200**, 566 (1950).
- (6) McGlashan, M.L., Potter, D.J.B., *Ibid.*, **A267**, 478 (1962).
- (7) McGlashan, M.L., Wormald, C.J., *Trans. Faraday Soc.* **60**, 646 (1964).
- (8) Orye, R.V., Prausnitz, J.M., *Ind. Eng. Chem.* **57**, 18 (May 1965).
- (9) Union Carbide Chemicals Co., "Alkyl and Alkylene Amines," New York, 1961.
- (10) Van Ness, H.C., "Classical Thermodynamics of Non-Electrolyte Solutions," Macmillan, New York, 1964.
- (11) Weissberger, A., Proskauer, E.D., Riddick, J.S., Toopes, E.E., Jr., "Organic Solvents," Interscience, New York, 1955.
- (12) Wilberg, K.B., "Laboratory Technique in Organic Chemistry," McGraw-Hill, New York, 1960.

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