

MOLECULAR INTERACTION IN BINARY LIQUID MIXTURES*

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Excess thermodynamic properties¹ of binary liquid mixtures are found to be considerably influenced by the interaction between the molecules of the components. When one of the components is in associated state, addition of the second (non-associated) component often brings about a decrease in association. This may however be followed by a combination due to interaction between the unlike molecules. As is well known, hydrogen bonding plays an important part in such association. Factors which influence the strength of the hydrogen bond may be expected also to affect the extent of association. Excess volumes of binary mixtures of *o*-toluidine as well as *m*-toluidine with cyclohexane, benzene, and dioxan have been measured and the results are interpreted on this basis.

Experimental

The toluidines (B.D.H. and E. Merck) were dried over caustic potash for about 24 hr and distilled twice.

Benzene (B.D.H.) was washed with concentrated sulphuric acid several times until no colour developed in the acid layer, then with dilute alkali, and finally with distilled water. It was dried over anhydrous calcium chloride for 2 days and distilled. The final distillation was carried out over phosphorus pentoxide.

Cyclohexane (B.D.H.) was washed several times with a cold mixture of concentrated sulphuric and nitric acids to nitrate any benzene present. After repeated washing with distilled water, it was dried and distilled and fractionated over sodium.

Dioxan was dried over caustic potash for 2 days and distilled over caustic potash. The sample distilling between 101° and 101.5° was collected, refluxed with metallic sodium for 6 hr, and distilled over it.

The samples had the following density values at 30°: cyclohexane 0.76904 (lit.² 0.76914); benzene 0.86817 (0.86836); dioxan 1.0222 (1.0223); *o*-toluidine 0.99017 (0.99037); *m*-toluidine 0.98081 (0.98097).

Excess volume is evaluated from the precision density measurements by the pyknometric method described by Naidu and Krishnan.³ Measurements have been made at $30 \pm 0.02^\circ$ and density values are reproducible to 1 part in 10^4 .

Results

The dependence of excess volume V^E on composition in the mixtures studied is represented by Figures 1 and 2. Curves in these figures may be represented by the equation:

$$V^E/X_A X_B = A + B(X_A - X_B) + C(X_A - X_B)^2 \quad (1)$$

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¹ Scatchard, G., *Chem. Rev.*, 1931, **28**, 321.

² Timmermans, J., "Physico-chemical Constants of Pure Organic Compounds." (Elsevier: New York 1950.)

³ Naidu, P. R., and Krishnan, V. R., *Trans. Faraday Soc.*, 1965, **61**, 1347.

Values of the constants A , B , and C , and excess volumes of the systems *o*-toluidine-cyclohexane, *o*-toluidine-benzene, *o*-toluidine-dioxan, *m*-toluidine-cyclohexane, *m*-toluidine-benzene, and *m*-toluidine-dioxan for equimolar mixtures are presented in Table 1.

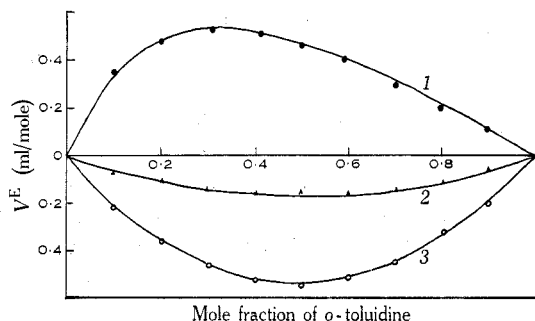
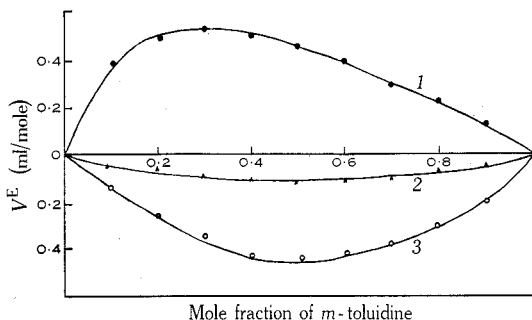


Fig. 1.— V^E values for mixtures of *o*-toluidine and 1, cyclohexane; 2, benzene; 3, dioxan.

Fig. 2.— V^E values for mixtures of *m*-toluidine and 1, cyclohexane; 2, benzene; 3, dioxan.



Discussion

In the mixtures of cyclohexane with the toluidines, the diluent (cyclohexane) causes breaking up of the associated toluidine molecules^{4,5} leading to a positive contribution to the excess volume. The observed values of excess volumes in the systems *o*-toluidine-cyclohexane and *m*-toluidine-cyclohexane are in agreement with this contention. In the binary liquid mixtures of toluidines with benzene and dioxan, the polymers of toluidines are broken up on dilution with benzene and dioxan, and this is followed by association between unlike molecules through the hydrogen bond interaction involving the hydrogen of the amino group and π -electrons of the benzene molecule and the lone-pair electrons of the oxygen of dioxan respectively. Values of excess volumes of the systems show that the effect of the interaction between unlike molecules on volume change is stronger than that of depolymerization of the solute molecules; this leads to a net contraction. The experimental results show that the interaction between toluidines and dioxan are stronger than between toluidines and

⁴ Gordy, W., and Stanford, S. C., *J. Am. chem. Soc.*, 1940, **62**, 497.

⁵ Medhi, K. C., Banerjee, S. B., and Kastha, G. S., *Indian J. Phys.*, 1962, **36**, 457.

benzene. The lone pair of electrons of oxygen in dioxan would definitely contribute to a greater hydrogen bond strength than the π -electrons of benzene. Comparison of V^E data of mixtures of *o*-toluidine with those of *m*-toluidine with benzene and dioxan would show the association effect on volume change is less for *m*-toluidine mixtures than for *o*-toluidine. *o*-Toluidine (pK_a 4.5) is known to be less basic than

TABLE I
EXCESS VOLUME V^E (ml/mole) AND CONSTANTS A , B , AND C

System	V^E	A	B	C
<i>o</i> -Toluidine-cyclohexane	+0.47	+1.789	-1.437	+1.295
<i>o</i> -Toluidine-benzene	-0.15	-0.637	-0.046	-0.086
<i>o</i> -Toluidine-dioxan	-0.55	-2.165	+0.149	+0.225
<i>m</i> -Toluidine-cyclohexane	+0.46	+1.789	-1.437	+1.295
<i>m</i> -Toluidine-benzene	-0.12	-0.490	-0.064	+0.256
<i>m</i> -Toluidine-dioxan	-0.44	-1.813	-0.042	+0.336

m-toluidine (pK_a 4.8); this indicates decreased electron availability on amino nitrogen and therefore a lower degree of association between unlike molecules through hydrogen bonding in the case of *m*-toluidine mixtures is to be expected. In the absence of any strong (hydrogen bond) interaction between cyclohexane and toluidines no differentiation between *o*- and *m*-toluidines is evident, but with the progressive increase of interaction from toluidine-benzene to toluidine-dioxan, the differentiation becomes more prominent as shown by the values for V^E .

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