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Received for review March 21, 1983. Accepted June 16, 1983.

Use of Mixing Rules in the Analysis of Data for Binary Liquid Mixtures

Tejraj M. Aminabhavi

Department of Chemistry, Karnatak University, Dharwad-580003, India

The binary mixture data of density and refractive index published earlier are further analyzed to test the validity of refractive index mixing rules. It is found that the Lorentz–Lorenz (LL), Gladstone–Dale (GD), Weiner, and Arago–Biot (AB) relations perform considerably well within the experimental precision. For the experimental systems studied here Heller's relation proved unsatisfactory.

Introduction

The literature dealing with the study of binary liquid mixtures has been extensive since the development of refractive index mixing rules (*1*). Among these, the most widely used relations are those of Lorentz-Lorenz (LL) and Galdstone-Dale (GD). These theoretical mixing rules have in common that they are based upon the electromagnetic theory of light with the implicit restriction that the molecules may be considered as dipoles or assemblies of dipoles induced by an external field. A series of failures of specific ones of these mixing rules reported in the literature is due to this restriction having been overlooked; others are due to the fact that other restrictions (homogeneous, undistorted electromagnetic field) had not been considered. The details of the relative merits and interrelations of a few mixing rules have been elegantly discussed by Heller (*1*).

One of the serious drawbacks of most of the mixing rules, however, is their inability to account for changes in volume and refractivity during mixing. A recent theory by Aminabhavi and Munk (*2*) provides an answer to this problem wherein the changes in volume and refractivity were adequately treated for six binary liquid mixtures from both density and refractive index data. In this work, as a part of the ongoing research program dealing with binary liquid mixtures, an attempt has been made to test several of the mixing rules using density and refractive index data published earlier (*3*).

Mixing Rules

One of the most frequently used mixing rules in the analysis of refractive index and density data of mixtures is due to Lorentz-Lorenz

$$\frac{n_{12}^2-1}{n_{12}^2+2}=\phi_1\left[\frac{n_1^2-1}{n_1^2+2}\right]+\phi_2\left[\frac{n_2^2-1}{n_2^2+2}\right] \qquad (1)$$

Here, n_{12}, n_1, and n_2 are the refractive indices of mixtures, solvent 1, and solvent 2, respectively, and ϕ_1 and ϕ_2 are the volume fractions of the respective components in the mixture. The volume fraction ϕ_i of the i-th component in the mixture is defined as $\phi_i \equiv C_i/\rho_i$ where C_i is the concentration (g/mL) and ρ_i is the density of the i-th component. Alternatively, $\phi_i = w_i\rho_{ij}/\rho_i$, where w_i is the weight fraction of the i-th component and ρ_{ij} is the density of the mixture.

The Gladstone-Dale (GD) relation has the following form:

$$n_{12}-1=\phi_1(n_1-1)+\phi_2(n_2-1) \qquad (2)$$

Several alternative forms of eq 1 and 2 have been given in the literature. However, the most frequently used relations are in terms of specific refractions (mL/g). In such a case, eq 1 and 2 take the following forms:

$$\left[\frac{n_{12}^2-1}{n_{12}^2+2}\right]\frac{1}{\rho_{12}}=\left[\frac{n_1^2-1}{n_1^2+2}\right]\frac{w_1}{\rho_1}+\left[\frac{n_2^2-1}{n_2^2+2}\right]\frac{w_2}{\rho_2} \qquad (3)$$

$$\frac{n_{12}-1}{\rho_{12}}=\left[\frac{n_1-1}{\rho_1}\right]w_1+\left[\frac{n_2-1}{\rho_2}\right]w_2 \qquad (4)$$

Weiner's relation which applies to isotropic bodies of spherically symmetric shape and which presupposes volume additivity is given in the following form:

$$\frac{n_{12}^2-n_1^2}{n_{12}^2+2n_1^2}=\phi_2\left[\frac{n_2^2-n_1^2}{n_2^2+2n_1^2}\right] \qquad (5)$$

Heller's relation which assumes the equivalence of the light scattering equations of Debye and Rayleigh has the following form:

$$\frac{n_{12}-n_1}{n_1}=\tfrac{3}{2}\phi_2\left[\frac{m^2-1}{m^2+2}\right] \qquad (6)$$

where $m = n_2/n_1$. Eq 5 and 6 differ from others by the absence of ϕ_1 in the formulation. They can therefore be strictly valid only in the case of volume additivity, i.e., if $\phi_1 = v_1^0/(v_1^0 + v_2^0)$, $\phi_2 = v_2^0/(v_1^0 + v_2^0)$ where superscript zero refers to volume of the components before mixing.

One other relation due to Arago and Biot (AB) has the following form:

$$n_{12}=\phi_1 n_1+\phi_2 n_2 \qquad (7)$$

It should be noted that the fundamental difference between eq

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Table I. Calculated Average Deviations of ΔN Using Different Mixing Rules

wavelength, nm	10^3(av deviation)				
	eq 3	eq 4	eq 5	eq 6	eq 7
Acetophenone (1)-Benzene (2)					
589	-2.42	-2.40	-1.80	-8.40	-1.90
546	0.50	0.60	1.10	-4.70	1.00
436	0.60	0.60	1.25	-5.30	1.20
Acetophenone (1)-Bromobenzene (2)					
589	-0.90	-1.20	-2.70	1.5	-2.70
546	2.20	1.90	0.50	0.55	0.46
436	2.30	2.00	0.50	5.3	0.50
Chlorobenzene (1)-Acetophenone (2)					
589	-1.90	-1.90	-1.7	0.90	-1.70
546	0.50	0.53	0.71	2.30	0.71
436	0.54	0.56	0.78	3.00	0.78
Toluene (1)-Acetophenone (2)					
589	-1.80	-1.80	-1.43	6.10	1.50
546	0.91	0.90	1.30	8.00	1.30
436	0.90	0.84	1.30	8.80	1.20
Bromobenzene (1)-Dimethyl Sulfoxide (2)					
589	2.40	1.84	1.54	-13.50	1.40
546	1.83	1.30	1.00	-14.00	0.90
436	2.00	1.30	1.10	-15.50	1.30
Dimethyl Sulfoxide (1)-Water (2)					
589	-3.50	-3.83	4.31	-21.49	4.00
546	-4.31	-4.64	3.58	-22.98	3.24
Chlorobenzene (1)-Benzene (2)					
589	-0.76	-0.73	-0.48	-4.69	-0.50
546	-0.54	-0.52	-0.27	-4.58	-0.57
436	-0.53	-0.53	-0.26	-4.67	-0.27
Chlorobenzene (1)-Carbon Tetrachloride (2)					
589	2.22	1.92	1.93	-9.79	1.87
546	2.21	1.91	1.91	-10.16	3.93
436	2.50	2.09	2.12	-11.48	2.03
Bromobenzene (1)-Benzene (2)					
589	-0.30	-0.50	-0.28	-10.82	-0.34
546	0.57	0.38	0.77	-9.91	0.71
436	-0.67	-0.88	-0.50	-11.64	-0.54
Chlorobenzene (1)-Bromobenzene (2)					
589	0.48	0.24	-0.47	6.08	-0.50
546	0.86	0.60	-0.13	6.36	-0.14
436	0.99	0.71	-0.01	6.87	-0.07

1 and 5 is that the reference dielectric constant in the latter equation is that of the solvent, n_1^2, while in the former reference it is that of the vacuum, $n_0^2 = 1.0$. When n approaches unity, eq 1 and 5 become identical.

All of the above relations are derived for strictly volume additivity (no changes in volume on mixing are assumed). Also, eq 2 reduces to eq 7 if one assumes volume additivity. However, the GD relation does not reduce to the AB equation if volume additivity is not assumed. In fact, the GD equation formulated for volume additivity is a limiting case of Heller's equation (eq 6).

Discussion of Results

In view of the availability of the earlier data (*3*), further experimentation appeared unnecessary. Thus, in this section, an attempt has been made to test the validity of mixing rules outlined in the previous section. This approach consisted of comparing the refractive index of mixtures determined experimentally with that calculated from the mixing rules. The difference in refractive index, ΔN, may be expressed as

$$\Delta N = N_{12}(\text{exptl}) - N_{12}(\text{calcd}) \qquad (8)$$

Using experimental values of densities and refractive indices, I calculated the value of N_{12} for all mixing rules (eq 3-7). The average deviations of the calculated values from the experimental ones are presented in Table I for 10 binary systems studied earlier.

Of the five mixing rules tested, except Heller's relation, the rest of them reproduced experimental data well within the limits of experimental precision. A close similarity was observed between the LL and GD relations as well as between the Weiner and AB relations. The observed poor fit (as evidenced by larger average deviation compared to other relations) in the case of Heller's relation may be due to the fact that this relation relies on the approximation $(m^2 - 1)/(m^2 + 2) \simeq (2m/3)(m - 1)$, i.e., $n_1 \simeq n_2$, whereas all other equations reduce correctly in the limiting cases. However, none of the above-mentioned mixing rules account for the changes in volume and refractivity during mixing of two liquids. It should be recalled that a rigorous analysis of the refractive index and density data were carried out in our previous papers (*2-4*) and thus it appears mandatory to treat the changes in volume and refractivity in the analysis of binary mixture data.

Conclusions

Previously published binary data of refractive index and density were further evaluated to test the validity of the existing mixing rules. It was found that the Lorentz-Lorenz, Gladstone-Dale, Arago-Biot, and Weiner relations were better in the analysis of data for binary mixtures. Heller's relation proved to be inaccurate in reproducing the experimental results.

Acknowledgment

I am extremely grateful to Professor Petr Munk of the University of Texas, Austin, for his constructive comments on this work.

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Received for review February 22, 1982. Revised manuscript received September 30, 1982. Accepted June 27, 1983.